In our earlier communication[41] we extrapolated our results obtained with 193 nm for Nb_xCN/Nb_xBr for $x \geq 2$ to give a monomer ratio Nb_1CN/Nb_1Br of approximately 15. That extrapolation may still be valid. The 193 nm might be a wavelength at which $\Phi_{(Nb_xCN)^+}/\Phi_{(Nb_xBr)^+} \approx 1$; thus the relative peak intensity ratio reflects the reaction cross section. Because the IP's of Nb_1Br and Nb_1CN are above 6.42 eV, one is not able to prove whether or not a good correlation can be made between the crossed-beam experiments and the cluster studies like the one presented. With the availability of tunable light sources in the wavelength region below 190 nm, one could try to softly ionize the niobium monomer products, hoping that the ionization cross sections of both products are not too different at that (these) wavelength(s). The 157-nm ionization laser is able to ionize all the Nb_xCN and Nb_xBr product clusters by one-photon absorption. However, its one-photon energy is ~3 eV higher than the average IP of the large clusters. This might leave their cluster ions electronically excited after ionization. The conversion of electronic excitation into vibration energy leads to internally hot cluster ions which can be cooled off by evaporating small neutral or ionic clusters. The unexpected $(Nb_1CN)^+/(Nb_1Br)^+$ value of less than unity could be explained by considering the following evaporation mechanism:

$$(Nb_xCN^+)^* \xrightarrow{\Phi_{1a}} Nb_{x-1}^+ + Nb_1CN \quad (1)$$
$$\xrightarrow{\Phi_{1b}} Nb_{x-1} + Nb_1CN^+$$
$$(Nb_xBr^+)^* \xrightarrow{\Phi_{2a}} Nb_{x-1}^+ + Nb_1Br \quad (2)$$
$$\xrightarrow{\Phi_{2b}} Nb_{x-1} + Nb_1Br^+$$

If other factors are equal, the ratio R could be determined by Φ_{1b}/Φ_{2b}. For the Nb_xP^+ fragment (where P can be either CN or Br), the branching ratio of NbP^+/Nb_{x-1}^+ depends on the inverse ratio of the IP's of the two neutral species (i.e., $IP_{Nb_{x-1}}/IP_{NbP}$). Niobium bromide, with the bromine atom having three pairs of nonbonding electrons, is expected to have a lower ionization potential than Nb_1CN. Due to back-donation from CN to the metal atoms, a slight positive charge can be created on the bonded niobium atom. This would increase the IP of the Nb_xCN product. Thus the ratio $R = \Phi_{1b}/\Phi_{2b} = IP_{Nb_1Br}/IP_{Nb_1CN}$ is less than unity, as observed. This conclusion is based on the assumption that the ionization cross sections of NbCN and NbBr are comparable. If this is not true, then the difference in their ionization cross sections could account for the observed product mass intensity ratio.

Possible Conclusions

In this paper, we have studied the reaction of BrCN with gaseous niobium clusters. Impulsive type collisions are expected to dominate in the reaction between BrCN and metallic *atoms*. This gives rise to the high value of the stereochemical selectivity ratio of MCN to MBr.[39,40] As the number of atoms in the cluster increases, it is expected that the nature of the collisions changes to the "sticky" type. This leads to a decrease in the selectivity ratio.

Of the four laser wavelengths used in this study, two are found to give results in agreement with this expectation. The other two, one with higher photon energy (157 nm) and the other with lower photon energy (218 nm), gave results that are not in agreement with our chemical intuition. This discrepancy again emphasizes the importance of the laser–cluster interactions during the one-photon ionization process and the absorption characteristics of the product cluster at the wavelength used. These effects could greatly modify the observed product distribution from that produced during the reaction being studied.

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Reduction Potentials of CO_2^- and the Alcohol Radicals

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Equilibrium constants were measured at 25 °C for the reactions $CO_2^{\bullet-} + Tl^+ \rightleftharpoons CO_2 + Tl^0$ (K = 0.2), $CH_2O^{\bullet-} + Tl^+ \rightleftharpoons CH_2O + Tl^0$ (K = 0.005), $CH_3CHO^{\bullet-} + Tl^+ \rightleftharpoons CH_3CHO + Tl^0$ (K = 0.53), and $(CH_3)_2CO^{\bullet-} + Tl^+ \rightleftharpoons (CH_3)_2CO + Tl^0$ (K = 520). These constants give reduction potentials for $CO_2^{\bullet-}$, $CH_2O^{\bullet-}$, $CH_3CHO^{\bullet-}$, and $(CH_3)_2CO^{\bullet-}$ of −1.90, −1.81, −1.93, and −2.10 V, and for $^\bullet CH_2OH$, CH_3CHOH, and $(CH_3)_3COH$ of −1.18, −1.25, and −1.39 V. All potentials are based on $E°(Tl^+/Tl_{aq}^0) = -1.94$ V. The stability constant for the reaction $Tl^0 + Tl^+ \rightleftharpoons Tl_2^+$ was found to be 140 M^{-1}. Values of ΔG_f^0 for the radicals in solution are given and values of $\Delta G_f°$ and $\Delta H_f°$ for the radicals in the gas phase are estimated based on the assumption that the free energy of solution of the neutral radicals is the same as for the corresponding alcohol or formic acid.

Introduction

Estimates of reduction potentials for $CO_2^{\bullet-}$ and the alcohol radicals are uncertain to at least ±0.2 V. Accurate measurements of these potentials relative to the Tl^+/Tl_{aq}^0 couple are presented here. Butler and Henglein[1] found that $CO_2^{\bullet-}$, $CH_3CHO^{\bullet-}$, and $(CH_3)_2CO^{\bullet-}$ reduced Tl^+ to Tl^0 and concluded that the reduction potentials of the radicals were more negative than the Tl^+/Tl^0 couple. Actually these reactions are expected to be reversible under accessible experimental conditions. Three equilibria will be involved for each radical

$$RO^{\bullet-} + Tl^+ \rightleftharpoons RO + Tl^0 \quad (1)$$
$$^\bullet ROH + OH^- \rightleftharpoons RO^{\bullet-} + H_2O \quad (2)$$
$$Tl^0 + Tl^+ \rightleftharpoons Tl_2^+ \quad (3)$$

where RO is CO_2, HCHO, CH_3CHO, or $(CH_3)_2CO$. The value of K_2 is known for each radical.[2-4] The dimer ion formation,

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TABLE I: Reduction Potentials[a]

RO^-	$E°(RO/RO^-)$	pK[b]	$E°(RO,H^+/{}^{\bullet}ROH)$
CH_2O^-	−1.81	10.71	−1.18
CH_3CHO^-	−1.93	11.51	−1.25
$(CH_3)_2CO^-$	−2.10	12.03	−1.39
CO_2^-	−1.90	1.4	−1.82

[a] In volts. [b] Reference 2 and (for ${}^{\bullet}COOH$) ref 4.

reaction 3, has been observed before,[5] but the equilibrium constant K_8 reported here is considerably different from earlier results.[1,5]

Butler and Henglein also pointed out that the Tl^+/Tl^0 reduction potential can be estimated with reasonable precision from $E°(Tl^+/Tl_{(m)}) = -0.336$ V,[6] $\Delta G_f°(Tl_g^0) = 35.24$ kcal/mol[7] (1.529 eV/mol), and the assumption that $\Delta G°(Tl_g^0 \rightarrow Tl_{aq}^0) = 0$. This assumption can be improved by noting that the free energy of solution of Hg_g^0, the left-hand neighbor of Tl in the periodic table, is +1.79 kcal/mol[8] (0.078 eV/mol) and that of the nearest rare gas, Rn, is +2.7 kcal/mol (from its solubility). We will assume that the free energy of solution of Tl_g^0 is the same as that of Hg_g^0, so $E°(Tl^+/Tl_{aq}^0) = -1.94$ V. An uncertainty of ±0.05 V will cover the range in free energy of solution of +2.9 to +0.6 kcal/mol. The reduction potentials for $RO/RO^{\bullet-}$ can then be calculated from

$$E°(RO/RO^{\bullet-}) = -1.94 - 0.0592 \log_{10} K_1 \qquad (4)$$

Experimental Section

The preparation of the $TlClO_4$ was described earlier.[9] Formaldehyde solutions were diluted from AR grade 37% solution and were standardized by the sulfite method[10] after standing for a few days. Eastman Kodak acetaldehyde and USP Punctilious 200 proof ethanol were used. All other reagents were AR grade. CO_2 solutions were prepared by flowing CO_2 and Ar into a mixing chamber before bubbling through the solution. The CO_2 fraction in the mixing chamber was measured by gas chromatography. The CO_2 concentration in a solution equilibrated with pure CO_2 is 0.033 M. Oxygen was removed from all other solutions by Ar bubbling.

Pulse radiolysis was performed by using 40–200 ns pulses of electrons from a 2-MeV Van de Graaff accelerator. The samples were thermostated at 25 °C. The optical path length was usually 6 cm, sometimes 2 cm. Between 5×10^{-8} and 3×10^{-7} M radicals were generated per pulse.

Results

The free radicals and Tl^0 were produced by pulse radiolysis of solutions containing Tl^+ with formate and CO_2, or with an alcohol (methanol, ethanol, 2-propanol) and the corresponding aldehyde or ketone. Ninety percent of the radicals produced in water radiolysis are about equally divided between e_{aq}^- and OH. The remaining 10% are H atoms (some H_2 and H_2O_2 are also formed). The reactions leading to ${}^{\bullet}ROH$, $RO^{\bullet-}$, and Tl^0 formation are

$$e_{aq}^- + Tl^+ \rightarrow Tl^0 \qquad (5)$$

$$e_{aq}^- + RO \rightarrow RO^{\bullet-} \qquad (6)$$

$$H + Tl^+ \rightarrow H^+ + Tl^0 \qquad (7)$$

$$H + RHOH \rightarrow H_2 + {}^{\bullet}ROH \qquad (8)$$

$$OH + RHOH \rightarrow H_2O + {}^{\bullet}ROH \qquad (9)$$

where RHOH represents the formate/formic acid or the alcohol. For ethanol and 2-propanol, 13% of OH radicals produce ${}^{\bullet}CH_2CH_2OH$ and ${}^{\bullet}CH_2CH(CH_3)(OH)$. These radicals are poor reductants and do not reduce Tl^+ or otherwise interfere with the equilibria. Concentration ratios were such that OH oxidation of aldehydes or acetone was negligible.

Hydroxyl oxidation of Tl^+ can be important at high Tl^+ concentration

$$OH + Tl^+ \rightarrow TlOH^+ \qquad (10)$$

The $TlOH^+$ reacts further[11] with OH^- to give $Tl(OH)_2$ in basic solution. Reaction 10 was minor (2% or less of total radicals) in the ethanol/acetaldehyde and 2-propanol/acetone systems but was important in formate/CO_2 and methanol/formaldehyde systems. Fortunately $TlOH^+$ and $Tl(OH)_2$ are strong oxidants and react further according to

$$Tl^{II} + RHOH \rightarrow Tl^{I} + {}^{\bullet}ROH + H^+ \qquad (11)$$

For instance, 75% of the OH radicals produced in solutions containing 10^{-2} M formate and 10^{-2} M Tl^+ oxidize Tl^+ to Tl(II). After this solution was pulsed, a prompt growth of Tl^0, Tl_2^+ was observed, due to reaction 5. Then there was a slower growth by a factor of 2.1 as CO_2^- reduces Tl^+. This is the factor expected if each OH produces a $CO_2^{\bullet-}$. A similar effect was observed for methanol solutions in the absence of formaldehyde, though the growth was not as clearly observed due to the slowness of the Tl^+ reduction by $CH_2O^{\bullet-}$. The Tl(II) disappearance was observed at 360 nm. Rate constants for reaction with methanol, ethanol, 2-propanol, and formaldehyde were 1×10^6 to 2×10^6 M^{-1} s^{-1}. Reaction with formate was faster but an intermediate complex with a 1×10^{-6} s lifetime was formed before decay to $CO_2^{\bullet-}$. The disappearance of Tl(II) and production of Tl^0 and ${}^{\bullet}ROH$ by reactions 5 and 9 were complete in a few microseconds, always a shorter time than required for equilibration of reaction 1.

The Equilibria. Alcohol radicals and CO_2^- exist in acid and base forms, which have different absorption spectra, and the effective extinction coefficient, ϵ_1, of an equilibrium mixture, will vary with OH^- concentration according to

$$\epsilon_1 = \frac{\epsilon_{RO\bullet^-} + \epsilon_{\bullet ROH}/K_2[OH^-]}{1 + 1/K_2[OH^-]} \qquad (12)$$

The CO_2^- studies performed here were done at 420 nm where absorption by $CO_2^{\bullet-}$ or ${}^{\bullet}COOH$ is a negligible part of the observed absorbances ($\epsilon_1 < 30$ M^{-1} cm^{-1}). The studies of alcohol radicals in basic solution were done at three wavelengths, 325, 420, and 450 nm, where $\epsilon_{RO\bullet^-} \gg \epsilon_{{}^{\bullet}ROH}$. Furthermore, absorbance by the radicals contributes very little to the observed absorbance; for instance, ϵ for $CH_3CHO^{\bullet-}$ is 600 M^{-1} cm^{-1} at 325 nm, 170 at 420 nm, and 70 at 450 nm.[12] In practice, ϵ_1 was usually left as a parameter to be determined at each wavelength and pH, but it could have been calculated or even taken as zero in all cases with little effect on the equilibrium constants obtained.

Reduced thallium exists in two forms, Tl^0 and Tl_2^+, and the effective extinction coefficient of an equilibrium mixture is

$$\epsilon_2 = \frac{\epsilon_{Tl^0} + \epsilon_{Tl_2}K_3[Tl^+]}{1 + K_3[Tl^+]} \qquad (13)$$

The observed absorbance per unit path length when all four species are present can be expressed by using an apparent extinction coefficient, ϵ_{app}

$$\epsilon_{app}([{}^{\bullet}ROH] + [RO^{\bullet-}] + [Tl^0] + [Tl_2^+]) = \epsilon_1([{}^{\bullet}ROH] + [{}^{\bullet}RO^{\bullet-}]) + \epsilon_2([Tl^0] + [Tl_2^+])$$

When all reactions are at equilibrium the radical and Tl^0, Tl_2^+

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concentrations can be expressed in terms of K_1, K_2, K_3, $[Tl^+]$, [RO], and $[OH^-]$ so that

$$\epsilon_{app} = \frac{\epsilon_1 + \epsilon_2 K_1([Tl^+]/[RO])f}{1 + K_1([Tl^+]/[RO])f} \tag{14}$$

where

$$f = \frac{1 + K_3[Tl^+]}{1 + 1/K_2[OH^-]}$$

It is convenient to present the data in terms of the fraction of total reduction that is present as the sum of Tl^0 and Tl_2^+. This fraction is $(\epsilon_{app} - \epsilon_1)/(\epsilon_2 - \epsilon_1)$ and eq 14 can be rearranged to give

$$\frac{\epsilon_{app} - \epsilon_1}{\epsilon_2 - \epsilon_1} = \frac{K_1([Tl^+]/[RO])f}{1 + K_1([Tl^+]/[RO])f} \tag{15}$$

In basic solutions reactions 2[2] and 3 are much faster than reaction 1 and may be treated as preequilibria. The rate of approach to equilibrium is thus expected to be first order with

$$k_{obsd} = k_1 \frac{K_2[OH^-]}{1 + K_2[OH^-]}[Tl^+] + k_{-1}\frac{[RO]}{1 + K_3[Tl^+]} \tag{16}$$

In practice, second-order reactions of the radicals and Tl^0 caused further slow changes in absorbance. This effect was minimized by using very low total radical concentrations and was corrected for by adding a term with constant slope α to the rate equation, that is

$$A = (A_0 - A_f)e^{-k_{obsd}t} + A_f + \alpha t \tag{17}$$

where A is the measured absorbance and A_0 and A_f are the initial absorbance and "final" absorbance extrapolated back to $t = 0$ with slope α. Extinction coefficients are calculated from A_f and the concentration of reduced species, which in turn is calculated from the energy delivered to the sample and the yield of reduction.

Dependence of Reduction Yield on Tl^+ Concentration. Free radical yields in pulse radiolysis studies are weakly dependent on the concentration of reactive solutes. A 10% variation between 10^{-4} and 0.1 M solutions is quite usual. The variation of total ($Tl^0 + Tl_2^+$) yield with Tl^+ concentration was measured here for one case, that of argon-saturated solutions of 0.5 M 2-propanol at pH 7 containing 5×10^{-5} M $Ru(bpy)_3^{2+}$ (bpy, 2,2′-bipyridine) and variable Tl^+. The Tl^0 and Tl_2^+ react rapidly with $Ru(bpy)_3^{2+}$

$$Tl^0 + Ru(bpy)_3^{2+} \rightarrow Tl^+ + Ru(bpy)_3^+ \tag{18}$$

$$Tl_2^+ + Ru(bpy)_3^{2+} \rightarrow 2Tl^+ + Ru(bpy)_3^+ \tag{19}$$

and so $Ru(bpy)_3^+$ yield at completion of reactions 18 and 19 is a measure of total Tl^0 formation. $Ru(bpy)_3^+$ has a strong absorption at 505 nm where its extinction coefficient is greater than that of $Ru(bpy)_3^{2+}$ by 1.1×10^4 M^{-1} cm^{-1}.[13] k_{18} and k_{19} were determined from the growth in absorption to be 1.0×10^{10} and 5×10^9 M^{-1} s^{-1}. The reactions lie far to the right and the 2-propanol radical, $^\bullet C(CH_3)_2OH$, does not reduce $Ru(bpy)_3^{2+}$. The relative reduction yields by e_{aq}^- in 2×10^{-4} M, 10^{-3} M, 10^{-2} M, and 0.1 M Tl^+ solutions were found to be 1.00, 0.984, 0.981, and 1.041, and were reproducible to 1%. If the $Ru(bpy)_3^+$ yield in 2×10^{-4} M Tl^+ solution is equated to the e_{aq}^- yield in 0.5 M 2-propanol in the absence of Tl^+, then the reduction yields are 3.15, 3.10, 3.09, and 3.28 atoms per 100 eV absorbed, respectively. The variation with concentration is real but small and it is assumed on this basis that total radical yields in the formate and basic alcohol solutions studied here, which include the $^\bullet$ROH and $RO^{\bullet-}$ yield, are independent of Tl^+ concentration. The constancy of the yields is all that is important, but the extinction coefficients were calculated with a total reduction yield of 7.0 radicals per 100 eV absorbed.

Tl^0–Tl_2^+ Equilibrium. In Tl^+ solutions, with 0.5 M 2-propanol present at pH 7, Tl^0 is formed by e_{aq}^- reduction, reaction 5, and all OH radicals end up as $^\bullet$ROH radicals by reactions 9 and 11.

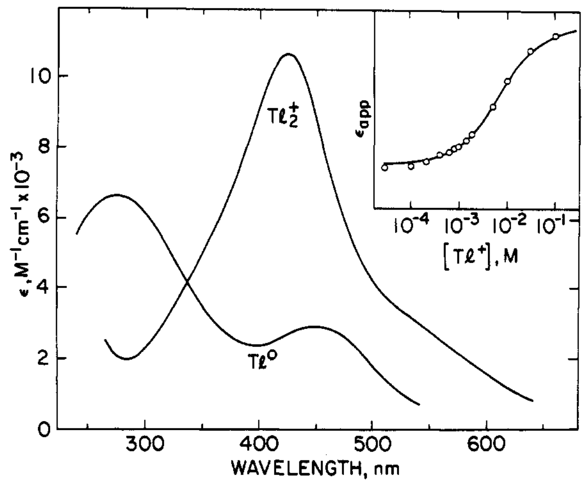

Figure 1. Spectra of Tl^0 and Tl_2^+. Inset: variation of ϵ_2 at 420 nm with thallous ion concentration. The curve is calculated for K_3 = 140 m^{-1}.

The $^\bullet$ROH radicals do not reduce Tl^+ at this pH or absorb light above 350 nm. The solutions used here are the same ones for which total $Tl^0 + Tl_2^+$ yields were reported in the previous section, so accurate yields are known or can be interpolated.

The effective extinction coefficient after equilibration, ϵ_2, should vary with Tl^+ concentration according to eq 13. The approach to equilibrium was nearly complete within an 80-ns pulse, but a small subsequent rise gave $k_{obsd} = 1.7 \times 10^7$ s^{-1} in 0.005 M Tl^+ solution. At the highest Tl^+ concentrations a subsequent small decrease in absorbance, at most 10%, occurred as hydrolyzed Tl(II), which absorbs weakly in this region, disappeared by reaction 11. k_{obsd} for this reaction was 7×10^5 s^{-1} and extinction coefficients were calculated at the end of this reaction. A later change, which was second order in Tl^0, was minimized by producing small Tl^0 concentrations, 5×10^{-7} M. The variation of ϵ_2 with $[Tl^+]$ is shown in Figure 1, from which K_3 = 140 M^{-1}. The statistical error is about ±5%. At 420 nm ϵ_{Tl^0} is found to be 2840 and $\epsilon_{Tl_2^+}$ is 11 700 M^{-1} cm^{-1}. The k_{obsd} of 1.7×10^7 s^{-1} gives $k_3 = 1.4 \times 10^9$ M^{-1} s^{-1} and $k_{-3} = 1 \times 10^7$ s^{-1}. The spectra of Tl^0 and Tl_2^+ derived from the data are also shown in Figure 1. The spectrum of $(CH_3)_2\dot{C}OH$, determined separately, has been subtracted from the observed spectra.

This value of K_3 is a factor of 16 smaller than that reported by Cercek et al.[5] and confirmed by Butler and Henglein.[1] The first study was made in the absence of alcohol and at decadic intervals of Tl^+ concentration. We have repeated this system and find data in good agreement with theirs. The difficulty lies in the analysis of the data. They assumed ϵ_{Tl^0} to be zero, ignored H atom reactions, and assumed a reduction yield varying strongly with Tl^+ concentration, which was shown here to be most unlikely. The rate constant for reaction 7 is 5×10^7 M^{-1} s^{-1},[14] so at 2×10^{-6} s after the pulse, when they collected their data, H atoms had not reacted in 10^{-3} M Tl^+ solution, had partially reacted in 10^{-2} M solution, and had completely reacted in 0.1 M solution. Furthermore, $Tl(OH)^+$ production was only partially complete as reaction 10 is an equilibrium reaction at low Tl^+. With reasonable corrections for these effects, their data and ours give K_3 to be about 120 M^{-1}, but the value is imprecise (±40%). It is clearly consistent with the value obtained here with alcohol present.

The disagreement with the later work[1] is more worrisome because the same system was studied by them as was studied here. The source of the discrepancy may lie in the time scale. They measured absorbance 10^{-5} s after the pulse. There is subsequent production of Tl_2 in these systems and we find this species to have a very intense absorption peak at 400 nm. Possibly a contribution from this absorption was erroneously attributed to Tl_2^+.

Acetone/$(CH_3)_2CO^{\bullet-}$ System. The pK of $(CH_3)_2\dot{C}OH$ is 12.03,[2] which gives K_2 = 93 M^{-1}. This value was confirmed here by following the rate of production of $Tl^0 + Tl_2^+$ at various $[OH^-]$

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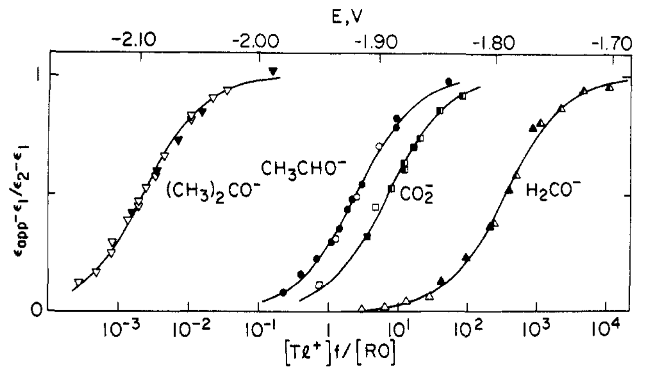

Figure 2. Variation of fraction of radicals present as Tl^0 and Tl_2^+ at equilibrium $[(\epsilon_{app} - \epsilon_1)/(\epsilon_2 - \epsilon_1)]$ with thallous ion and RO concentrations. Curves are calculated fits to eq 16. Key: for $(CH_3)_2CO^{\bullet-}$ (RO = $(CH_3)_2CO$), ▽ = 1×10^{-4} M Tl^+, ▼ = 4×10^{-4} M Tl^+; for $CH_3CHO^{\bullet-}$ (RO = CH_3CHO), ○ = 3×10^{-4} M Tl^+, ● = 1×10^{-3} M Tl^+; for $CO_2^{\bullet-}$ (RO = CO_2), □ = 0.01 M Tl^+, ■ = 0.025 M Tl^+, ◨ = 0.04 M Tl^+; for $H_2CO^{\bullet-}$ (RO = total formaldehyde), △ = 0.03 M Tl^+, ▲ = 0.08 M Tl^+, ◭ = 0.19 M Tl^+.

in the absence of acetone. In these solutions k_{obsd} is given by the first term of eq 16, and the best fit gave $K_2 = 90$ M^{-1}. TlOH is reported[15] to have a stability constant of 6 M^{-1}, so the rest of the studies here were performed at OH^- concentrations below 10^{-2} M to avoid complications due to TlOH. When acetone was present the [acetone]/[Tl^+] ratio was between 10 and 500, so most e_{aq}^- reacted with acetone by way of reaction 6. The absorption before equilibration is due to $^{\bullet}$ROH and $RO^{\bullet-}$ and is very small. The final absorption is mainly due to Tl^0 and Tl_2^+, so good growth kinetics were observed at all concentration ratios. k_{obsd} was measured in solutions containing 0.002 and 0.01 M OH^- and fit to eq 16, from which $k_1 = 7.1 \times 10^9$ M^{-1} s^{-1} and $k_{-1} = 1.6 \times 10^7$ M^{-1} s^{-1}. This value of k_1 is more than twice the value reported for pH 13, 2.0×10^9 M^{-1} s^{-1}. Ionic strength differences can account for about a factor of 1.5. The ratio of k_1 to k_{-1}, one estimate of K_1, is 450.

The dependence of $(\epsilon_{app} - \epsilon_1)/(\epsilon_2 - \epsilon_1)$ on solution composition is shown in Figure 2. The fitted value of ϵ_1 in 0.002 M OH^- at 325 nm was 340 M^{-1} cm^{-1}, and ϵ_1 was 0 in 0.01 M OH^- at 450 nm. The errors are about ± 100 M^{-1} cm^{-1}. ϵ_2 in 10^{-4} M Tl^+ was 3090 M^{-1} cm^{-1} at 450 nm and 4140 M^{-1} cm^{-1} at 325 nm, and in 4×10^{-4} M Tl^+ at 450 nm it was 3170 M^{-1} cm^{-1}. These values are 3% larger, 13% smaller, and 2% smaller, respectively, than those calculated from the spectra of Figure 1 and eq 13. The value of K_1 calculated from eq 15 by using these data is 440, in agreement with the kinetic results. The average ionic strength of these solutions was 0.006 M, so the activity coefficients of Tl^+ and $(CH_3)_2CO^-$ ions are expected to be 0.92.[16] The value of K_1 at zero ionic strength is thus expected to be 520 at 25 °C. This value of K_1, with eq 4, gives $E°((CH_3)_2CO/(CH_3)_2CO^{\bullet-}) = -2.10$ V.

Acetaldehyde/CH_3CHO^- System. The pK of $CH_3\dot{C}HOH$ is 11.51,[2] so $K_2 = 310$ M^{-1}. As with the acetone system, this value of K_2 was confirmed by studying the [OH^-] dependence of the rate of reduction of Tl^+ by CH_3CHO^- in the absence of acetaldehyde, and the value found was $K_2 = 300$ M^{-1}. When acetaldehyde was added, the [CH_3CHO]/[Tl^+] ratio varied from 0.02 to 3, so most e_{aq}^- reduced Tl^+ to Tl^0 and roughly equal quantities of CH_3CHO^- and $Tl^0 + Tl_2^+$ are formed initially. At low ratios, the absorbance approximately doubles as the radical reduces Tl^+ and at high ratios, the absorbance disappears as the Tl^0, Tl_2^+ portion reduces CH_3CHO to CH_3CHO^-. Kinetics were determined in these two regions and k_{obsd} fit to eq 16. The value of k_1 was 4.7×10^8 M^{-1} s^{-1} and k_{-1} was 1.0×10^9 M^{-1} s^{-1}. The literature value of k_1 is 1.5×10^9 M^{-1}. The reason for the difference is not clear. The ratio of k_1/k_{-1} is 0.47.

At intermediate ratios of CH_3CHO to Tl^+ there is very little change of absorbance with time and the data cannot be fit independently to eq 17. The difficulty is solely in the determination of k_{obsd}, however, and k_{obsd} can be interpolated from rate studies at higher and lower ratios by use of eq 16. With k_{obsd} known A_f can be determined from eq 17 and the resulting values of $(\epsilon_{app} - \epsilon_1)/(\epsilon_2 - \epsilon_1)$ are shown in Figure 2. The fitted values of ϵ_1 in 0.01 M OH^- were 580 M^{-1} cm^{-1} at 325 nm and 0 at 450 nm. ϵ_2 was 3870 M^{-1} cm^{-1} at 325 nm in 3×10^{-4} M Tl^+ and 4050 M^{-1} cm^{-1} at 325 nm, 3550 M^{-1} cm^{-1} at 450 nm in 1×10^{-3} M Tl^+. These values for ϵ_2 are 18% smaller, 13% smaller, and 3% smaller than those expected from the spectra of Figure 1 and eq 13. The best value of K_1 is 0.43. Ionic strength was 0.01 M, so activity coefficients are 0.90 and K_1 is expected to be 0.53 at zero ionic strength. This value and eq 4 gives $E°(CH_3CHO/CH_3CHO^{\bullet-}) = -1.93$ V.

Formaldehyde/$CH_2O^{\bullet-}$ System. The pK of $^{\bullet}CH_2OH$ is 10.71[2] and was not measured here. Our studies were performed in 0.01 M NaOH, so the radical was 95% ionized. The reduction of Tl^+ by $CH_2O^{\bullet-}$ has not been previously reported, possibly because both k_1 and k_{-1} are very small. It was necessary to use large concentrations of Tl^+ and formaldehyde to equilibrate the solution rapidly enough to avoid serious complications from the second-order reactions. The Tl^+ concentration was in the range of 0.03–0.19 M, and even then the ratio α/A_0, which has units of s^{-1}, was as much as 15% of k_{obsd}. Ionic strength was kept constant at 0.2 M in these studies by adding $NaClO_4$. The reduction of Tl^+ to Tl^0 and Tl_2^+ can be clearly seen in solutions with 0.5 M methanol, 0.19 M Tl^+, and 10^{-3} M formaldehyde and below, and somewhat less clearly in 0.08 M Tl^+ solutions in the same range. The reverse reaction can be followed when the formaldehyde to Tl^+ ratio is greater than 0.1. The kinetics were not described well by eq 16, but required an additional reaction, probably

$$CH_2O^{\bullet-} + 2Tl^+ \underset{}{\overset{k_{1a}}{\rightleftharpoons}} CH_2O + Tl_2^+ \qquad (20)$$

Here, CH_2O is used to represent formaldehyde, but it is realized that it is actually mainly $CH_2(OH)_2$ in solution at the concentrations used.[17] Reaction 20 does not introduce any new equilibrium constant as K_{1a} is K_1K_3, but it does introduce a new rate term. The expression for k_{obsd} with reactions 1 to 3 and 20 is

$$k_{obsd} = (k_1[Tl^+] + k_{1a}[Tl^+]^2)\left\{1 + \frac{k_{-1}}{k_1}\frac{[RO]}{[Tl^+](1 + K_3[Tl^+])}\right\} \qquad (21)$$

where RO is $CH_2(OH)_2$. The best fit of the rate data to eq 21 gave $k_1 = 1.5 \times 10^4$ M^{-1} s^{-1}, $k_{1a} = 3.3 \times 10^5$ M^{-2} s^{-1}, and $k_{-1} = 6 \times 10^6$ M^{-1} s^{-1}, or $K_1 = 0.0025$.

Many of the solutions of interest for measuring ϵ_{app} are in the intermediate concentration ratio range where there is little difference between A_0 and A_f. As with acetaldehyde solutions, k_{obsd} was calculated, in this case from eq 21, and used to determine the best values of A_0 and A_f from the data and eq 17. The resulting values of $(\epsilon_{app} - \epsilon_1)/(\epsilon_2 - \epsilon_1)$ are shown in Figure 2. The fitted value of ϵ_1 was 900 ± 200 M^{-1} cm^{-1} at 420 nm, 0.01 M OH^-. Only part of this absorption is due to $CH_2O^{\bullet-}$ for which ϵ_1 was found to be 320 M^{-1} cm^{-1} at 420 nm. The wavelength dependence of the remainder was measured in 0.03 M Tl^+, 2 M methanol solutions with 0.1 M formaldehyde present. The results were not very precise but the portion of the absorbance not due to $CH_2O^{\bullet-}$ had an absorption maximum around 400 nm and is probably Tl_2, formed by Tl^0 recombination in a "spur" reaction. Such reactions are expected at the high Tl^+ concentrations used here. The value of ϵ_2 at 420 nm was 10 800 M^{-1} cm^{-1} in 0.19 M Tl^+, 3% larger than expected from Figure 1 and eq 13. The value of K_1 was found to be 0.0031, and the agreement with the value from the kinetics is satisfactory. The activity coefficients[16] of Tl^+ and $CH_2O^{\bullet-}$ are each expected to be about 0.73 at 0.2 M ionic strength, so K_1 at zero ionic strength should be about 0.005. This value corresponds

(15) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4.
(16) $\log_{10} \gamma = 0.5(\mu^{1/2}/(1 + \mu^{1/2}) - 0.2\mu)$.
(17) Reference 10, p 53.

TABLE II: Free Energies of Formation, Heats of Formation, and Bond Strengths[a]

radical	$\Delta G_f°$(aq)[b]	$\Delta G_f°$(g)[g]	$\Delta H_f°$(g)[g]	$\Delta H_f°$(g) lit.[h]	D(H–ROH)[g]
$^{\bullet}CH_2OH$	−2.2[c]	+1.0	−3.4	−6.2 ± 1.5	96.7[j]
$^{\bullet}CH(OH)CH_3$	−3.6[d]	−0.5	−11.6	−15.2 ± 1	96.7
$^{\bullet}C(OH)(CH_3)_2$	−6.6[e]	−3.6	−22.8	−26.6 ± 1.1	94.4
$^{\bullet}COOH$	−50.3[f]	−45.2	−47.0	−53.3[i]	95.6

[a] In kcal/mol. [b] From eq 22. [c] $\Delta G_f°[CH_2O]_{gas} = -24.5$ (ref 18); $\Delta G_{sol}°[CH_2O]_g = -4.9$ (ref 10, p 112). [d] $G_f°[CH_3CHO]_{gas} = -30.81$ (ref 18); $\Delta G_{sol}°[CH_3CHO]_g = -1.6$ (ref 19). [e] $\Delta G_f°[(CH_3)_2CO]_{gas} = -36.50$ (ref 20); $\Delta G_{sol}°[(CH_3)_2CO]_g = -2.1$ (ref 19). [f] $\Delta G_f°[CO_2]_{aq} = -92.26$ (ref 18). [g] From eq 23–25. [h] Reference 24. [i] Reference 23. [j] Possible errors in $^{\bullet}CH_2OH$ values are discussed in the text.

to $E°(CH_2(OH)_2/CH_2O^{\bullet -}) = -1.81$ V.

$CO_2/CO_2^{\bullet -}$ System. The pK of $^{\bullet}COOH$ is 1.4[4] ($K_2 = 4 \times 10^{12}$ M^{-1}). All solutions used here were at pH 3.7, so $K_2[OH^-]$ is 200 and the reciprocal is negligible compared to 1. The kinetics of approach to equilibrium was studied in solutions containing 0.01–0.04 M Tl^+. The best fit was to eq 21 where RO is now CO_2, which gave $k_1 = 3.0 \times 10^6$ M^{-1} s^{-1}, $k_{1a} = 2 \times 10^7$ M^{-2} s^{-1}, and $K_1 = 0.10$. The fit to eq 16 was slightly worse, but gave $k_1 = 3.8 \times 10^6$ M^{-1} s^{-1} and $k_{-1} = 3.5 \times 10^7$ M^{-1} s^{-1}, or $K_1 = 0.11$. Kinetic data were available at low and high $[CO_2]$ to $[Tl^+]$ ratio, but not in the middle region.

Values of $(\epsilon_{app} - \epsilon_1)/(\epsilon_2 - \epsilon_1)$ are plotted in Figure 2. The best fitted value of ϵ_1 was 0, but few data were collected at low $[Tl^+]/[CO_2]$, so ϵ_1 could be several hundred. The effect on K_1 of assuming that $\epsilon_1 = 300$ would be about 6% which is about the statistical error of the determination. ϵ_2, based on a reduction yield of 7.0 radicals per 100 eV, was 10% lower than expected at all Tl^+ concentrations, from Figure 1 and eq 13. This discrepancy is likely due to the assumption that the radical yield is the same in 5×10^{-3} M formate solution as it is in 0.5–2 M alcohol solution. The value of K_1 is found to be 0.15, 40% higher than the kinetically determined value. The difference between the two values is slightly larger than might be expected but is probably not significant. The ionic strength of the solutions was maintained at 0.05 M with $NaClO_4$, so activity coefficients should be 0.82, or K_1 at zero ionic strength is 0.2. This value gives $E°(CO_2/CO_2^-) = -1.90$ V.

Discussion

The values of $E°(RO/RO^-)$ determined here are collected in Table I. Reduction potentials of the neutral radicals are also given in Table I, calculated from

$$E°(RO,H^+/^{\bullet}ROH) = E°(RO/RO^{\bullet -}) + 0.0592\ \mathrm{p}K\ (^{\bullet}ROH)$$

The experimental errors are small, about ±0.01 V for $CH_2O^{\bullet -}$ and $CO_2^{\bullet -}$ and less than ±0.005 V for the other two and are probably close to the relative errors in the $E°$ values. The errors in the absolute values are ±0.05 V because of the uncertainty in the estimate of $\Delta G°$ for $Tl_g^0 \rightarrow Tl_{aq}^0$.

The potentials for $^{\bullet}CH_2OH$ and $CH_2O^{\bullet -}$ are referred to aqueous formaldehyde, which is a complex mixture.[17] In a 1 M solution, about 15% of the formaldehyde is present as polymer and 0.05% as HCHO. The rest is methylene glycol, $CH_2(OH)_2$. Another estimate of the fraction present as unhydrated HCHO can be made from the data presented here. It seems reasonable to assume the reaction of Tl^0 with unhydrated HCHO is diffusion-limited, that is k is about 5×10^9 M^{-1} s^{-1}. The rate measured for the less exoergic reactions with acetaldehyde and acetone support this assumption. It also seems reasonable to assume that Tl^0 does not react with polymer or methylene glycol. Hence, the ratio of the observed rate constant for Tl^0 reducing total formaldehyde, 6×10^6 M^{-1} s^{-1}, to the diffusion-limited rate constant should be a measure of the fraction of total formaldehyde present as unhydrated HCHO. The value so obtained, 0.001, is in good agreement with the above literature value, 5×10^{-4}.

The free energies of formation of the aqueous radical in kilocalories per mole can be calculated from

$$\Delta G_f°(^{\bullet}ROH)_{aq} = \Delta G_f°(RO)_{aq} - 23.05E°(RO,H^+/^{\bullet}ROH) \quad (22)$$

where $\Delta G_f°(RO)_{aq}$ is the free energy of formation of aqueous HCHO, CH_3CHO, $(CH_3)_2CO$, or CO_2, values of which are available in standard references.[18–20] The free energies so calculated are given in Table II.

Much of the literature on the thermodynamics of these radicals is concerned with species in the gas phase. A reasonable route from aqueous solution data to gas-phase estimates is to assume that the free energy of solution of the radicals from the gas phase into water is the same as that of the parent compound

$$\Delta G°_{sol}(^{\bullet}ROH) \approx \Delta G°_{sol}(RHOH)$$

These values are −3.20,[18] −3.15,[18] −3.0,[19] and −5.1[18,20] kcal/mol for methanol, ethanol, 2-propanol, and formic acid. The formic acid value is nearly the same as that for acetic acid, −5.38 kcal/mol,[18] so it is apparent that these free energies of solution depend mainly on the functional group and the approximation probably introduces negligible error. Thus

$$\Delta G_f°(^{\bullet}ROH)_{gas} \approx \Delta G_f°(^{\bullet}ROH)_{aq} - \Delta G°_{sol}(RHOH) \quad (23)$$

$$\Delta H_f°(^{\bullet}ROH) = \Delta G_f°(^{\bullet}ROH) + T\Delta S_f°(^{\bullet}ROH) \quad (24)$$

and bond dissociation energies can be calculated

$$D(\text{H–ROH}) = \Delta H_f°(^{\bullet}ROH)_{gas} + \Delta H_f°(H^{\bullet}) - \Delta H_f°(ROH) \quad (25)$$

The entropy $S°(^{\bullet}COOH)$ has been calculated to be 59.85 eu[21] and $S°(^{\bullet}CH_2OH)$ has been calculated to be 57.89 eu.[22]

The application of difference methods[23] for the entropies of the other two alcohol radicals suggests that $S°(^{\bullet}ROH) - S°(RHOH)$ should be nearly the same for $^{\bullet}CH(OH)CH_3$ as for $^{\bullet}CH_2OH$, which is +0.6 eu, but should be about 1 eu less for $^{\bullet}C(OH)(CH_3)_2$, so $S°[^{\bullet}CH(OH)CH_3]$ is taken as 68 eu and $S°[^{\bullet}C(OH)(CH_3)_2]$ is taken as 74 eu. Errors of 2 eu, which are reasonable, would correspond to errors in $\Delta G°$ of ±0.6 kcal/mol. Heats of formation of the alcohols and formic acid are available in standard references.[18] Estimates for $\Delta G_f°(^{\bullet}ROH)_{gas}$, $\Delta H_f°(^{\bullet}ROH)_{gas}$, and D(H–RH) calculated by using eq 23–25 are given in Table II along with literature values for $\Delta H_f°(^{\bullet}OH)$.[23,24]

Two serious problems are apparent in Table II. First, the $\Delta H_f°$ gas-phase values estimated here are higher by 3–6 kcal/mol than earlier literature estimates. Second, the normal progression expected in D(H–ROH) going from primary to secondary to tertiary bonds is about −2 kcal per step and is not observed between $^{\bullet}CH_2OH$ and $^{\bullet}CH(OH)CH_3$, though it is observed between $^{\bullet}CH(OH)CH_3$ and $^{\bullet}C(OH)(CH_3)_2$.

The latter problem is one of relative $E°$ values and so systematic errors in $E°(Tl^+/Tl^0)$ or in free energies of solution of $^{\bullet}ROH$ are

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not involved. The reality of the expected −2 kcal/mol differences is supported by rate constants for reactions of H atoms

$$H + RHOH \rightarrow H_2 + {}^{\bullet}ROH \quad (26)$$

which are in the ratios 1:6.5:29[25] for methanol, ethanol, 2-propanol. The differences in free energies of activation for these reactions are obtained from $\Delta(\Delta G^{\ddagger}) = RT \ln$ (ratio), which is 1.1 kcal/mol for $\Delta G^{\ddagger}$(methanol) − $\Delta G^{\ddagger}$(ethanol) and 2.0 kcal/mole for $\Delta G^{\ddagger}$(methanol) − $\Delta G^{\ddagger}$(2-propanol). These reactions are mildly exothermic and so $\Delta G^{\ddagger}$, should vary with $^1/_2\Delta G°$ for H–ROH bond dissociation, which is about the same as differences in D(H–ROH) for alcohols. Thus expected bond energy differences are −2.2 kcal/mol between $^{\bullet}CH_2OH$ and $^{\bullet}CH(OH)CH_3$ and −4 kcal/mol between $^{\bullet}CH_2OH$ and $^{\bullet}C(OH)(CH_3)_2$. The origin of the discrepancy is most likely that $\Delta H_f°(^{\bullet}CH_2OH)$ in Table II is low. The $H_2CO^{\bullet-}$, Tl^+ equilibrium was the most difficult to observe, both because of reaction rates and because of concentration ranges and, hence, has the largest error of the four reported here. However, the curve for $CH_2O^{\bullet-}$ in Figure 1 would have to be shifted to the right a factor of 30 in the concentration ratio scale in order to accommodate a −2 kcal/mol error. This shift is far beyond any reasonable source of error unless there is a complete misinterpretation of the data. Indeed no reduction of Tl^+ by $CH_2O^{\bullet-}$ could have been observed in any solution studied here if the curve were actually that far to the right, whereas reduction was clearly seen in the solutions represented by the uppermost points on the curve. The source of the error is at least equally likely to be in the free energy of formation of formaldehyde in aqueous solution used here. This is certainly less well established than that of acetaldehyde, acetone, or CO_2, both because of possible errors in measurements of its vapor pressure above dilute aqueous solutions and because $\Delta H_f°$(HCHO) was in serious dispute until two recent values agreed well with each other.[26] We conclude that the values of $E°(CH_2O/CH_2O^{\bullet-})$ and $E°(CH_2O,H^+/^{\bullet}CH_2OH)$ given in Table I are the best available, but that $\Delta G_f°$ and $\Delta H_f°$ of $^{\bullet}CH_2OH$ in Table II are too negative by about 2 kcal/mol.

The 4 kcal discrepancy between values of $\Delta H_f°$ estimated here and earlier values in the literature could involve an error in the calculated $E°(Tl^+/Tl^0)$, but if this is the sole or even principal source of the error, the potential would have to be 0.17 V lower, or −1.77 V. The most uncertain element in the calculation of the potential is $\Delta G°_{sol}(Tl^0)_{gas}$, which would have to be −2.2 kcal/mol to produce this value, instead of the +1.8 kcal/mol based on Hg. The −2.2 kcal value would be almost as negative as that for hydrogen bonded hydroxylic molecules such as the lower alcohols (−3 kcal/mol), and so this explanation seems unreasonable.

Some recent papers have derived values of $D(H–RCH_3)$ for hydrocarbons from several different thermal decomposition reactions and find they are all consistent with $D[H–C_2H_5]$ = 100.7 kcal/mol,[27] $D[H–CH(CH_3)_2]$ = 99.3 kcal/mol,[28] and $D[H–C(CH_3)_3]$ = 96.7 kcal/mol.[28] Two lines of evidence indicate that our $\Delta H_f°$ and D(H–ROH) values are consistent with expectations based on these values. First, the literature values of $\Delta H_f°$ for the alcohol radicals in Table II were obtained from iodination kinetics.[23] The above dissociation energies for hydrocarbons were each about 4 kcal/mol greater than others based on iodination of the hydrocarbons, the same difference observed here. Second, aqueous solution H atom reaction rate constants with methanol, ethanol, and 2-propanol (reaction 26) are the same within experimental error as those with the corresponding hydrocarbon, ethane, propane, and 2-methylpropane.[25] Thus rate constant vs $\Delta G°$ relations would give $\Delta G°$ for dissociation of $H–CH_3OH$, the same as that for $H–CH_2CH_3$, for $H–CH(OH)CH_3$, the same as for $H–CH(CH_3)_2$, etc. The entropy differences $S°(^{\bullet}RCH_3) - S°(HRCH_3)$[23,28] are about 5 eu greater than $S°(^{\bullet}ROH) - S°(HROH)$, so bond dissociation energies of H–ROH are each expected to be about 1.5 kcal less than for the corresponding $H–RCH_3$. Comparison of the values from Table II with the $D(H–RCH_3)$ values given above indicate $D[H–CH(OH)CH_3]$ is 2.6 kcal/mol less than $D[H–CH(CH_3O_2)]$ and $D[H–C(OH)(CH_3)_2]$ is 2.3 kcal/mol less than $D[H–C(OH)(CH_3)_2]$, in adequate agreement with the expected 1.5 kcal.

The earlier value for $\Delta H_f°(^{\bullet}COOH)$[23] was based on the rate of thermal decomposition of benzeneacetic acid at 900 °C[29] and the assumption that the reaction rate is limited by bond cleavage. The expected products from H atoms from subsequent thermal decomposition of $^{\bullet}COOH$ were not found,[29] so perhaps the reaction does not involve bond cleavage at all. Note that with $\Delta H_f°(^{\bullet}COOH)$ = −47 kcal/mol, D(H–OCO) is only 5 kcal/mol. The activation energy for decomposition would be higher, however, as the bent $^{\bullet}COOH$ must attain linear geometry to produce CO_2.

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Registry No. $CH_2O^{\bullet-}$, 27837-46-3; $CH_3CHO^{\bullet-}$, 60427-04-5; $(CH_3)_2CO^{\bullet-}$, 17836-38-3; $CO_2^{\bullet-}$, 14485-07-5; $^{\bullet}CH_2OH$, 2597-43-5; $^{\bullet}CH(OH)CH_3$, 2348-46-1; $^{\bullet}C(OH)(CH_3)_2$, 5131-95-3; $^{\bullet}COOH$, 2564-86-5; Tl^+, 22537-56-0.

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