deductions based solely on upfield chemical shifts of coordinated olefinic protons, and we feel that the similarity to the h^4-C$_8$H$_8$M(CO)$_3$ (M = Fe, Ru) complexes provides compelling evidence in favor of the first interpretation. This similarity is further emphasized by the observation that peaks A, B, and D in the nmr spectrum of 2 collapse more rapidly than peak C as the temperature is raised from −140° (Figure 2). Provided the assignments of the two low-field multiplets are correct, this implies that a sequence of 1,2 shifts is responsible for the proton averaging, as found for h^4-C$_8$H$_8$M(CO)$_3$ (M = Fe, Ru)[8] and h^5-C$_5$H$_5$Fe(CO)$_2$-h^1-C$_5$H$_5$.[13]

Finally, we confirm the observation[16] that 1 in solution shows four bands (cm^{-1}) due to C–O stretching modes at 1970 (6), 1961 (10), 1914 (4), and 1899 (8) (each ±3 cm^{-1}), instead of the expected two, indicating the presence of conformers similar to those postulated for complexes of the type h^5-C$_5$H$_5$Mo(CO)$_2$-h^3(allyl).[17,18] However, the conformer ratio may obviously vary with temperature since the low-temperature nmr spectrum indicates the presence of only one species. In agreement with this, we find that the bands at 1970 and 1914 cm^{-1} in the infrared almost disappear at ∼−60°. The present results do not enable us to decide which is the most stable conformer of the complex 1.

(16) R. B. King, *Inorg. Chem.*, 5, 2242 (1966).
(17) A. Davison and W. C. Rode, *ibid.*, 6, 2124 (1967).
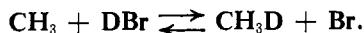(18) J. W. Faller and M. J. Incorvia, *ibid.*, 7, 841 (1968).

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Absolute Rate Constants for Radical–Molecule Reactions over a Wide Temperature Range:
CH$_3$ + DBr $\rightleftarrows$ CH$_3$D + Br.
The Heat of Formation and Entropy of the Methyl Radical

Sir:

The rates of virtually all radical–molecule reactions are measured relative to competitive radical reactions, most commonly radical–radical recombination.[1] We wish to report that we have measured the absolute rate constant for the reaction

$$CH_3 + DBr \longrightarrow CH_3D + Br \qquad (a)$$
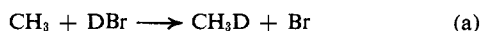
The accuracy of rate constants derived from competitive studies are limited by the accuracy to which the rate constant of the competing reaction is known. This constraint has been removed from the results reported here.

Our method gives direct access to the back reaction rate constants in atom-abstraction studies in which a radical and stable molecule are produced.[2] The availability of Arrhenius parameters for forward and back reaction rate constants provides values for the heats of formation and entropies of free radicals. As

(1) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Reactions," NSRDS-NBS 9, National Bureau of Standards, Washington, D. C., 1967.
(2) First report of this new technique: S. W. Benson, D. M. Golden, and R. Jackson, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, Abstract No. S191.

has already been pointed out,[3] kinetic studies provide the most practical approach to obtaining the thermodynamic functions of free radicals. Our apparatus is a modified version of one already described in detail, VLPP.[4]

We do not presently have the capability of measuring radical concentrations directly, as reported by Lossing and others.[5,6] Chemical stoichiometry is used instead. The decomposition of *t*-butyl peracetate (tBPA) was used at the highest temperature (1000°K) to provide 2CH$_3$ + acetone + CO$_2$. The acetone (Ac) and CO$_2$ are measured absolutely and thus yield rates of CH$_3$ production. The decomposition of di-*t*-butyl peroxide (dtBP) to give 2CH$_3$ + 2Ac was then used at all five temperatures (1000 to 608°K). Its higher vapor pressure makes it a more convenient methyl radical source in flow experiments. The results of the tBPA experiments confirmed that Br atoms were not abstracting hydrogen from acetone under our experimental conditions. Results based on acetone and CO$_2$ were identical.

These methyl radical sources were introduced at flow rates corresponding to 0.5 to 5 × 10^{16} molecules/sec of methyl radicals into the stirred flow reactor.[4] The source flow rate was held approximately constant during any one set of experiments. Decomposition was nearly 100%, except at 608°K. At this lowest temperature dtBP was approximately 70% decomposed. DBr was added at flow rates ranging from 1 to 150 × 10^{15} molecules/sec.

In the stirred flow reactor used here, it may be shown that

$$\frac{k_{eac}(Ac)}{k_{emed}(CH_3D)} = 1 + \frac{k_{eme}}{k_a(DBr)} \qquad (1)$$

where k_{eac}, k_{emed}, and k_{eme} are the first-order, apparent rate constants for escape from the Knudsen reaction cell[4] of acetone, CH$_3$D (MeD), and CH$_3$ radicals (Me), respectively. They are known accurately from the dimensions of the reaction cell.[7] (Ac), (CH$_3$D), and (DBr) are the steady-state concentrations of the respective species which are measured directly by our mass spectrometer. It follows from eq 1 that a plot of (Ac)/(CH$_3$D) against 1/(DBr) should give a straight line which may be used to obtain the desired rate constant k_a.

The reduced results are given in Figure 1. Results below 10% titration are not shown so that the fit to eq 1 could be shown at all temperatures conveniently in one figure. However, those results were included in computing the average rate constant.

C$_2$H$_6$ formation is not significant under the conditions of our experiment, but there is an appreciable quantity of CH$_3$Br formed at very high DBr flow rates and the

(3) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinetics*, 1, 217 (1969).
(4) S. W. Benson and G. N. Spokes, *J. Am. Chem. Soc.*, 89, 2525 (1967). VLPP represents the technique of very low pressure pyrolysis.
(5) F. P. Lossing and A. W. Thickner, *J. Chem. Phys.*, 20, 907 (1952), and subsequent papers.
(6) (a) E. Hedaya and D. W. McNeil, *J. Am. Chem. Soc.*, 89, 4213 (1967); (b) C. L. Angell, D. McLeod, Jr., and E. Hedaya, *ibid.*, 89, 4214 (1967); (c) E. Hedaya, *et al.*, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract No. ORGN 46.
(7) Note that $k_{eac}/k_{emed} = (17/58)^{1/2}$, the square root of the molecular weight ratio, and $k_{eme} = 1.03T^{1/2}$ for our 30-ml vessel with 2.05-mm diameter exit aperture.[4]

Table I. Rate Constants, k_a, and Arrhenius A factors

Temp, °K	Slope ($\pm \sigma$) $\times 10^{17}$	$10^{-8}k_a$, M^{-1} sec^{-1}	Log A for $E_a = 1.5$ kcal/mole	E_{act} for log $A = 8.8$ kcal/mole
608	0.289 ± 0.120	1.61	8.75	1.6
661	0.198 ± 0.050	2.57	8.90	1.1
773	0.303 ± 0.094	1.97	8.71	1.7
786	0.379 ± 0.194	1.59	8.61	2.1
1000	0.403 ± 0.103	1.91	8.61	2.3

steady-state (CH$_3$) concentration must be corrected for this. CH$_3$Br formation presumably arises from CH$_3$ reaction either with chemisorbed Br atoms at the wall, or homogeneously from Br$_2$, formed from wall recombination of Br atoms.
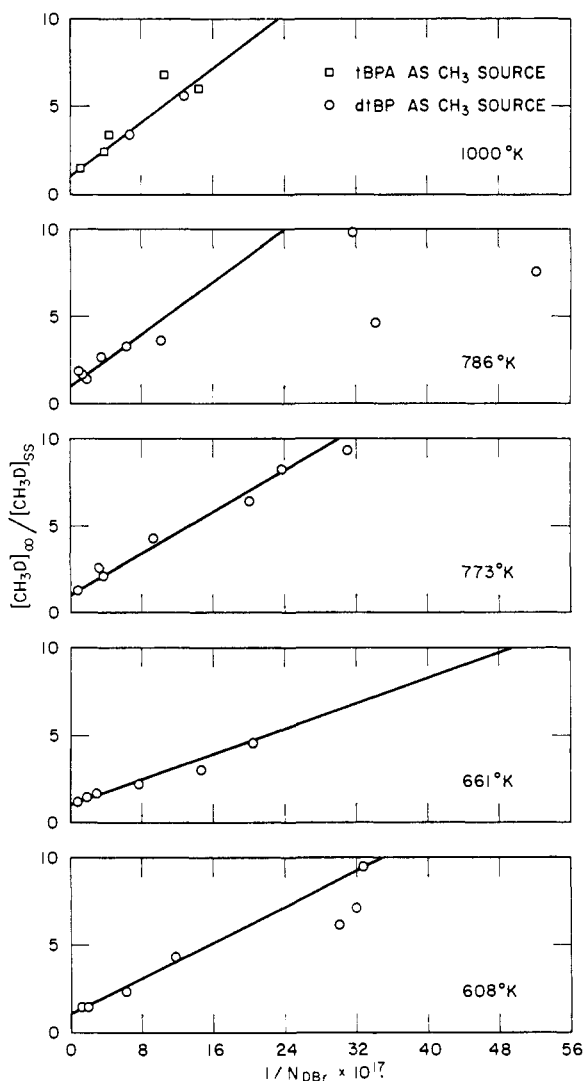

Figure 1. Normalized titration curve: (fraction titrated)$^{-1}$ $vs.$ (steady-state DBr flow)$^{-1}$. Note: Points below 10% titration are not shown. The lines are drawn to include them.

Good mass balance checks were provided by the relation $N^0_{DBr} - N_{CH_3D} = N_{DBr}$, where N^0_{DBr} is the measured rate of introduction of DBr.

Table I gives the slopes of the lines in Figure 1. All points were weighted equally. Estimated errors are one standard deviation. The computed Arrhenius parameters given in the last columns are discussed below.

A combination of thermochemical and photolysis studies[8] on the reaction

$$Br + CH_4 \longrightarrow HBr + CH_3 \qquad (-b)$$

has given

$$\log k_{-b} = 10.86 \, (\pm 0.39) - [(18.2 \pm 0.8)/\theta]$$

where $\theta = 2.303RT$ in kcal/mole and k_{-b} is in l./(mole sec). At 800°K ($\theta = 3.65$ kcal/mole), log $k_{-b} = 5.88$. Using estimated values[9] for $C_p°$ and $S°$ for CH$_3$, and the known values of $\Delta H_f°$ and $C_p°$ and $S°$ for all other species,[9] we calculate $\Delta S_{-b(800)} = 8.8$ gibbs/mole, $\Delta H_{-b(800)} = 17.3$ kcal/mole, and $K_{-b} = 10^{-2.82}$. This gives for the reverse rate constant, $k_b = k_{-b}/K_{-b} = 10^{8.70}$ l./(mole sec). This is within a factor of 2.5 of the value $k_a = 10^{8.3}$ measured by us (Table I). For very exothermic reactions, such as (b) and (a), with very small activation energies, one expects a very small isotope effect with k_H/k_D of about 1.5.[1] The observed ratio $k_a/k_b = 2.5$ is in good agreement with this, within the experimental accuracy of the two separate measurements and the uncertainty in the thermochemical data.

If one assumes $k_H/k_D = 1.5 \pm 0.5$, and the known[9] $\Delta H_f°$(CH$_3$), then one can calculate from the above data a value of $S°_{300}$(CH$_3$) $= 45.3 \pm 0.8$ gibbs/mole, in excellent agreement with the estimated value of 46.1. If, instead, one uses the estimated $S°_{300}$(CH$_3$), one can calculate a value of $\Delta H_f°_{300}$(CH$_3$) $= 33.9 \pm 0.7$ kcal/mole in excellent agreement with current values.

In the temperature range of our experiments, the observed activation energy $E_a = 0 \pm 1$ kcal. From the observed kinetic and thermochemical data on reaction $-b$, we can deduce an expected value of $E_a = 1.5 \pm 0.9$ kcal/mole. Over our temperature range, this would result in a variation in k_a of a factor of 1.6, which is at present just within the experimental scatter. As seen from Table I, such an activation energy leads to an A factor for k_a of $A_a = 10^{8.75 \pm 0.15}$ l./(mole sec), in excellent agreement with the value deduced from the thermochemistry and the measured k_{-b}, namely $A_a = 10^{8.8 \pm 0.39}$. Alternatively, if we use this estimated A factor, we find the values for E_a shown in Table I, 1.7 ± 0.6 kcal/mole.

These measurements indicate that it is possible to measure radical-molecule rate constants over a large temperature range with reasonable accuracy. There is good reason to believe the precision can be appreciably improved. We are currently extending our measurements to higher temperatures and are attempting to improve signal-to-noise ratio problems by converting our present Polaroid camera-oscilloscope recorder arrangement to a slower scanning X-Y recorder system.

(8) G. B. Kistiakowsky and E. R. Van Artsdalen, $J.$ $Chem.$ $Phys.$, **12**, 469 (1944).

(9) S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968.

(10) Postdoctoral Research Associate.

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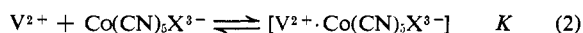# Electron-Transfer Reactions of Vanadium(II) and Some Monosubstituted Pentacyanocobaltate(III) Ions[1]

Sir:

Previous studies have shown that the reactions of the type in eq 1 generate $Co(CN)_5^{3-}$ as a metastable inter-

$$Co(CN)_5X^{3-} + V^{2+} + 5H^+ = Co^{2+} +$$
$$V^{3+} + X^- + 5HCN \quad (1)$$
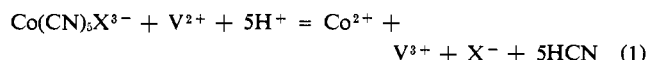
mediate.[2] The finding of $Co(CN)_5^{3-}$ does not in itself establish all the details of the mechanism, however, for it might have resulted as the primary product of an inner-sphere reaction ($\rightarrow Co(CN)_5^{3-} + V(H_2O)_5X^{2+}$), and it would also be the likely substance formed in an outer-sphere reaction, resulting from the rapid decomposition of the low-spin six-coordinate Co(II) complex $Co(CN)_5X^{4-}$. Whereas the mechanism of electron transfer has been classified unambiguously[3–6] as inner sphere or outer sphere for the reactions of many oxidizing agents with Cr^{2+}, $Co(CN)_5^{3-}$, and Ru-$(NH_3)_6^{2+}$, the question remains unresolved for but a few reactions of $V(H_2O)_6^{2+}$.[7–10] Evidence has been obtained in this study that the reactions in eq 1 proceed by inner-sphere (ligand bridged) mechanisms.

Rate studies have been carried out on the initial oxidation–reduction stage of the reactions in eq 1 for $X = Cl^-, Br^-, I^-, -SCN^-, N_3^-$, and H_2O. The reactions were measured at wavelengths permitting the following of both the loss of the complex, $Co(CN)_5X$ ($X = Br^-, I^-, -SCN^-$, and N_3^-), and the formation of the intermediate ($X = Br^-, Cl^-, H_2O$) with time. The rates which were evaluated by both stopped-flow and conventional spectrophotometric methods were found not to follow a simple second-order rate law. The second-order rate constants calculated from kinetic data taken with V^{2+} in considerable excess were found to decrease with increasing V^{2+} concentration. The reactions appeared to proceed with ion-pair formation according to the mechanism

$$V^{2+} + Co(CN)_5X^{3-} \rightleftharpoons [V^{2+}\cdot Co(CN)_5X^{3-}] \quad K \quad (2)$$

$$[V^{2+}\cdot Co(CN)_5X^{3-}] \longrightarrow Co(CN)_5^{3-} + V^{3+} + X^- \quad k \quad (3)$$

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2494.
(2) K. M. Davies and J. H. Espenson, *Chem. Commun.*, 111 (1969).
(3) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966), and references therein.
(4) J. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).
(5) J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964).
(6) R. C. Patel and J. F. Endicott, *ibid.*, **90**, 6364 (1968).
(7) B. R. Baker, M. Orhanović, and N. Sutin, *ibid.*, **89**, 722 (1967).
(8) J. H. Espenson, *ibid.*, **89**, 1276 (1967).
(9) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).
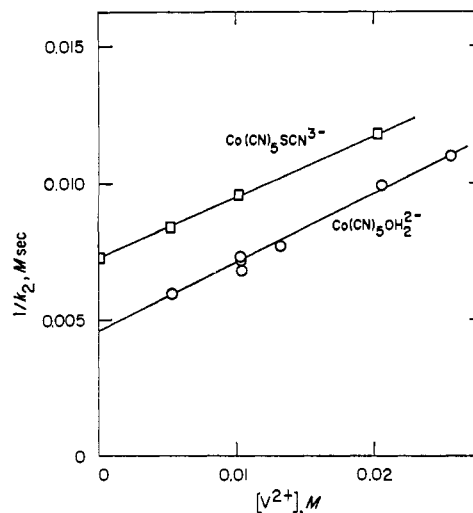(10) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

Figure 1. Illustrating the dependence of the apparent second-order rate constant on [V^{2+}] at 25.0° and $\mu = 1.00\ M$: upper line, $Co(CN)_5SCN^{3-}$; lower line, $Co(CN)_5OH_2^{2-}$.

According to this sequence, the second-order rate constant k_2 is $kK/(1 + K[V^{2+}])$. Linear plots of $1/k_2$ vs. [V^{2+}] were obtained in accord with this formulation; typical data are shown in Figure 1. Table I summarizes

Table I. Rate Parameters for the Reactions of V^{2+} and $Co(CN)_5X^{3-}$ at 25.0° and $\mu = 1.00\ M^b$

X	λ, nm	kK, M^{-1} sec^{-1}	k, sec^{-1}	K, M^{-1}
Cl$^-$	280	278	6.4	44
Br$^-$	280–300–050	168	c	c
Br$^-$ ^{a}	280	363	3.4	107
I$^-$	500	121	5.7	21
-SCN$^-$	264	138	4.5	31
-SCN$^-$ ^{a}	264	256	3.3	78
N$_3^-$	383	112	c	c
H$_2$O	280	218	4.1	53

^{a} $\mu = 0.200\ M$. ^{b} [H$^+$] $\sim \mu$, except for $Co(CN)_5N_3^{3-}$, where [H$^+$] was 0.100 M at $\mu = 1.00\ M$. ^{c} Under the conditions employed $K[V^{2+}]$ was very small compared to unity; hence only the product kK and not the separate values were obtained.

the values of the rate parameters for each complex.

The similarity in the values of k found for the different complexes suggests that the rate is controlled primarily by the loss of a water molecule coordinated to V^{2+}. Similar effects have been noted in earlier studies.[9] The range of values of the limiting second-order rate constant kK (120–260 M^{-1} sec^{-1}) is somewhat higher than the values[10] noted for other reactions (8–45 M^{-1} sec^{-1}). This is not surprising considering the charge types in the present reaction give rise to more favorable ion-pair formation.

For the complexes $Co(CN)_5N_3^{3-}$ and $Co(CN)_5SCN^{3-}$ direct proof of an inner-sphere mechanism was obtained in studies carried out at 350–360 nm where the V(III) complexes VN_3^{2+} and $VNCS^{2+}$ have absorption maxima.[11] At these wavelengths the transmittance–time oscillograms indicated not only the presence of the usual $Co(CN)_5^{3-}$ intermediate[2] and its slow decom-

(11) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).