Oxidations of Amines. IX. Correlation of Rate Constants for Reversible One-Electron Transfer in Amine Oxidation with Reactant Potentials

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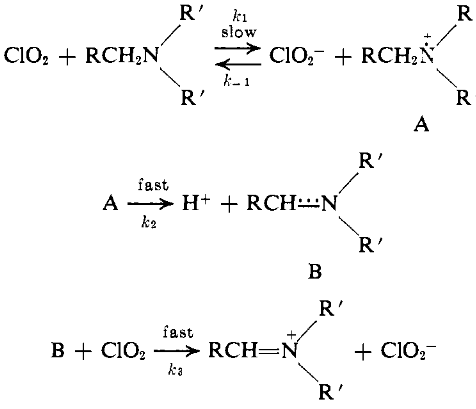
Abstract: A correlation between the logarithms of the rate constants for triethylamine oxidation by several oxidants and the oxidation potentials of the oxidants has been found. These oxidants include chlorine dioxide, permanganate, ferric, molybdicyanide, ferricyanide, and several ferric phenanthroline complexes. Also correlations for predicting the rates of amine oxidations from the oxidation potentials of the oxidants and the photoionization potentials or $\Sigma\sigma^*$ of the amines have been developed. Strong retardation by ferrocyanide in the oxidation of triethylamine by ferricyanide has been observed.

In previous papers[1,2] we have presented evidence for a reversible one-electron transfer step that is rate controlling in the oxidations of amines by chlorine dioxide.



The rates of amine oxidation by chlorine dioxide are dependent on inductive effects, *i.e.*, $\Sigma\sigma^*$, of the substituents on the amines.[1g] Values of $\Sigma\sigma^*$ have been shown to be proportional to the photoionization potentials[3] and also to the polarographic half-wave peak potentials[1g] of amines.

Several examples of relationships between the rates of oxidation–reduction reactions and the oxidation or reduction potentials of the reactants have been reported.[4] It has been postulated that such a correlation is with the free-energy change for the individual reaction step whose rate is being measured, rather than with the over-all free-energy change for the reaction process.[5,6] This paper will present evidence for a direct relationship between the rate of triethylamine oxidation and values of the oxidation potential, $E°$, for reversible one-electron oxidants. Also, further evidence for the reversibility of rate-determining one-electron transfer steps in amine oxidations will be given.

Experimental Section

Materials. Water triply distilled from neutral potassium permanganate was used throughout. The amine hydrochlorides were purified by repeated recrystallization from isopropyl alcohol to give purities greater than 99.8%, as measured by vapor phase chromatography of the free bases. Potassium octacyanomolybdate(IV) dihydrate was prepared by the method of Furman and Miller[7] and dried at 105° to constant weight. A solution of this salt, of known concentration, was added to excess lead dioxide in sulfuric acid, shaken for several minutes, and filtered to prepare a solution of octacyanomolybdate(V) of the same concentration. Substituted iron(II) phenanthroline complexes were obtained from the G. Frederick Smith Chemical Co.; the iron(III) complexes were obtained by the lead dioxide–sulfuric acid procedure.

Oxidation of Triethylamine by Ferricyanide and Its Retardation by Ferrocyanide. The kinetics were followed by measuring the absorbancy of potassium ferricyanide at 420 mμ on a Cary Model 14 recording spectrophotometer. The retarding effect of ferrocyanide was measured by adding varying amounts, up to 10^{-3} *M*, of potassium ferrocyanide to a reaction mixture consisting of 0.30 *M* triethylamine hydrochloride, 10^{-4} *M* $K_3Fe(CN)_6$, and 0.01667 *M* borate buffer at 25.0 ± 0.1°, pH 8.80, and 1.008 ionic strength adjusted with sodium chloride. The kinetics of ferricyanide reactions appear to be complicated by an equilibrium between ferricyanide ion and the ion pair, $KFe(CN)_6^{2-}$, as well as by a corresponding equilibrium for ferrocyanide ion, in which the ion pair is even more favored.[8] These ion pairs cause a salt effect on the oxidation potential of the ferriferrocyanide couple.[9] The oxidation potential for the experimental conditions used was calculated from equations in ref 9. We have observed specific salt effects on the

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(1) Papers of this series: (a) I, D. H. Rosenblatt, A. J. Hayes, Jr., B. L. Harrison, R. A. Streaty, and K. A. Moore, *J. Org. Chem.*, **28**, 2790 (1963); (b) II, D. H. Rosenblatt, L. A. Hull, D. C. De Luca, G. T. Davis, R. C. Weglein, and H. K. R. Williams, *J. Amer. Chem. Soc.*, **89**, 1158 (1967); (c) III, L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *ibid.*, **89**, 1163 (1967); (d) IV, W. H. Dennis, Jr., L. A. Hull, and D. H. Rosenblatt, *J. Org. Chem.*, **32**, 3783 (1967); (e) V, D. H. Rosenblatt, G. T. Davis, L. A. Hull, and G. D. Forberg, *ibid.*, **33**, 1649 (1968); (f) VI, G. T. Davis and D. H. Rosenblatt, *Tetrahedron Letters*, 4085 (1968); (g) VII, L. A. Hull, G. T. Davis, D. H. Rosenblatt, and C. K. Mann, *J. Phys. Chem.*, **73**, 2142 (1969); (h) VIII, L. A. Hull, D. H. Rosenblatt, W. P. Giordano, G. T. Davis, C. K. Mann, and S. B. Milliken, *ibid.*, **73**, 2147 (1969).

(2) It has been brought to our attention that the labeling of the rate constants in our previous papers (ref 1a–c) is misleading. The k_1 rate constants actually refer to the rate of disappearance of chlorine dioxide which equals two times the rate constant for disappearance of amine. The k_1 in the mechanism scheme refers to $k_{\text{amine}} = k_{ClO_2}/2$.

(3) We have calculated the equation IP = $1.23\Sigma\sigma^* + 7.69$ with a correlation coefficient of 0.93 from the data in (a) J. J. Kaufman and W. S. Koski, *J. Amer. Chem. Soc.*, **82**, 3262 (1960); (b) H. K. Hall, Jr., *ibid.*, **79**, 5441 (1957).

(4) (a) A summary of references on this subject has been given by J. H. Baxendale and S. Lewin, *Trans. Faraday Soc.*, **42**, 126 (1946); (b) D. H. Irvine, *J. Chem. Soc.*, 2977 (1959); (c) J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **50**, 808 (1954); (d) M. H. Ford-Smith and N. Sutin, *J. Amer. Chem. Soc.*, **83**, 1830 (1961).

(5) H. Gershinowitz, *J. Chem. Phys.*, **4**, 363 (1936).

(6) R. A. Marcus, *ibid.*, **26**, 872 (1957), and previous papers cited therein.

(7) N. H. Furman and C. O. Miller, *Inorg. Syn.*, **3**, 160 (1950).

(8) W. A. Eaton, P. George, and G. I. H. Hanania, *J. Phys. Chem.*, **71**, 2016 (1967).

(9) B. Mohai, S. Papp, and M. Sándor, *Veszpremi Vegyip. Egyet. Kozlemen.*, **8**, 121 (1964).

reaction of $K_3Fe(CN)_6$ with triethylamine (Table I).[10] A slow reaction, possibly ligand exchange, which resulted in a new shoulder in the 410- and 420-mμ absorbancy range was observed when potassium ferrocyanide was mixed with triethylamine in borate buffer. This reaction was too slow to interfere under the conditions used for ferricyanide kinetics. The ratio k_2/k_{-1} for ferrocyanide retardation (where k_2 is the forward irreversible step and k_{-1} is the backward reversible step) was estimated to be 1.3×10^{-5} M from the relationship[1c] $t_{1/2}[R_3N]/0.693 = (k_{-1}/k_1k_2)[Fe(CN)_6^{4-}] + 1/k_1$.

Table I. Salt Effects on Ferricyanide Oxidation of 0.2 or 0.3 M Triethylamine at pH 8.6–8.9

Ionic strength[a]	k_1, M^{-1} hr^{-1}
0.208	1.75
0.508	1.74
1.008	3.43
1.808	4.37

[a] The cation was almost entirely sodium (except for 3×10^{-4} M potassium) and the anion was chloride.

Kinetics of Substituted Ferric Phenanthrolines with Triethylamine. The kinetics of oxidation of triethylamine by several substituted ferric phenanthrolines were measured by following the appearance of the corresponding ferrous phenanthrolines at the following wavelengths: unsubstituted phenanthroline, 510 mμ; 5-methyl, 516 mμ; 4,7-dimethyl, 510 mμ; 5,6-dimethyl, 512 mμ; and 3,4,7,8-tetramethyl, 500 mμ. The kinetics of all of the phenanthrolines with the exception of the tetramethyl derivative were run at pH's between 1.45 and 2.00 using sulfuric acid as buffer. Kinetic experiments were carried out on 2.786 M triethylamine hydrochloride solutions at 25.0 ± 0.1°, and an ionic strength of 2.9 with 2×10^{-5} M ferric phenanthroline and 0.0186 M sulfuric acid. Experiments on unsubstituted and ferric 5-methylphenanthroline were run in 2.3 M triethylamine nitrate at ionic strength 2.36 to compare the influence of nitrate with that of chloride on the rate constant. A specific salt effect was found, in that the calculated bimolecular rate constant was higher in the presence of nitrate ion than it was in the presence of chloride ion. Unsubstituted ferric phenanthroline complex gave k_1 values (M^{-1} sec^{-1}) of 1.94×10^6 and 4.48×10^6 in 2.8 M chloride and 2.4 M nitrate solutions, respectively; and ferric 5-methylphenanthroline complex gave k_1 values of 1.49×10^6 and 4.53×10^6, respectively, in the same anion solutions. However, it was not convenient to find experimental conditions to demonstrate a rate dependency on anion throughout the range of anion concentrations. Increasing the anion concentration by added salt appeared to have no effect on the bimolecular rate constant. Probably the specific salt effect is caused by an ion pair between the ferric phenanthroline and the anion.[11] The pH and high amine concentrations were chosen to minimize the effects of side reactions, since ferric phenanthrolines are more stable and the ferrous phenanthrolines less stable in acid solution.[11-13] Ferrous phenanthroline decay appears to be an acid-catalyzed dissociation with loss of phenanthroline.[12] Ferric phenanthrolines may decay to olation products.[14] The kinetics of the triethylamine oxidation by ferric 3,4,7,8-tetramethyl-1,10-phenanthroline complex (9.0×10^{-6} M) were determined in 0.133 M acetate buffer, pH 4.27, 25.0 ± 0.1°, 1.03 ionic strength, and 0.90 M triethylamine. This reaction was run in acetate buffer because the ferrous complex was not stable enough at pH 2. This was possible as the ferric complex is much more stable than the other ferric phenanthroline complexes at pH 4. There was a slight decay of the ferric complex to a colorless product (*i.e.*, no absorbancy at 500 mμ); however, over 90% of the reaction proceeded by reduction of ferric 3,4,7,8-tetramethyl-1,10-phenanthroline by triethylamine. The oxidation potentials[15] of the ferric phenanthroline complexes are from the literature.[16]

Kinetics of Triethylamine Oxidation by Potassium Octacyanomolybdate(V). The kinetics of triethylamine oxidation by octacyanomolybdate(V) (molybdicyanide) were run in 0.020 M phosphate buffer, 0.2 ionic strength, 25.0 ± 0.1°, pH 6.66, 0.0040 M triethylamine, and 1×10^{-4} M $Mo(CN)_8^{3-}$. The reaction was followed by taking aliquots and stopping the reaction by addition of acid. A 100-fold excess of N,N,N′,N′-tetramethyl-*p*-phenylenediamine dihydrochloride in acid was added. The concentration of the resulting Würster cation radical was immediately measured at 560 mμ.[17] This analytical procedure did not work when a large excess (100-fold) of the reduced species, $Mo(CN)_8^{4-}$, was present. The N,N,N′,N′-tetramethyl-*p*-phenylenediamine dihydrochloride was quickly oxidized by air, so that it was necessary to work rapidly and to check blanks periodically in order to minimize errors from air oxidation. The oxidation potential of the molybdicyanide–molybdocyanide couple was calculated from equations[18] for ionic strength effects.

Data from the Literature. The kinetic constants for amine oxidation by chlorine dioxide and permanganate have been reported previously.[1] Holst determined the oxidation potential of the chlorine dioxide–chlorite couple.[19] The oxidation potentials for permanganate and the ferrous–ferric couple was taken from Latimer.[20,21] The mechanism and kinetics of hydrazine oxidation by ferric ion in water were determined by Higginson and Wright.[22] The electron impact ionization potential of hydrazine was determined by mass spectrometry.[23] The photoionization potentials of the amines were measured by Watanabe and Mottl.[24] Required $\Sigma\sigma^*$ values were obtained from ref 3b.

Theory

Marcus[6] formulated a theory which roughly predicts the rate of oxidation for redox systems which involve little molecular orbital overlap of the reactants. However, this utilizes the relationship $\Delta F° = nF(E°_{\text{oxidant}} - E°_{\text{reactant}})$. Unfortunately, oxidation potentials for irreversible systems such as those involving aliphatic amines cannot be determined.[25] Attempts to estimate such potentials have been made for a variety of other compounds.[26]

We tried to use the photoionization potentials, IP, of amines[27] in the gas phase as a way of indirectly estimating their oxidation potentials. In order to obtain the oxidation potential from the ionization potential, it is necessary to correct for solvation energy. One way of estimating this is by using the Born equation[28] for

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(10) Specific salt effects on the kinetics have been observed for other reactions with potassium ferricyanide: (a) H. B. Friedman and B. E. Anderson, *J. Amer. Chem. Soc.*, **61**, 116 (1939); (b) D. G. Lambert and M. M. Jones, *ibid.*, **88**, 4615 (1966).

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(13) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *ibid.*, 70, 2348 (1948).

(14) A. Gaines, Jr., L. P. Hammett, and G. H. Walden, Jr., *ibid.*, **58**, 1668 (1936).

(15) The pH and ionic strength effects on the oxidation potential of ferric phenanthroline have been determined by P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959).

(16) The oxidation potentials are found in ref 4d, with the exception of the ferric 4,7-dimethyl-1,10-phenanthroline complex, whose potential was taken from W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

(17) L. Michaelis, M. P. Schubert, and S. Granick, *J. Amer. Chem. Soc.*, 61, 1981 (1939).

(18) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, 40, 247 (1936).

(19) G. Holst, *Svensk Papperstid.*, **48**, 23 (1945); *Chem. Abstr.*, **39**, 3194 (1945).

(20) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1961, p 239.

(21) Reference 20, p 223.

(22) W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1551 (1955).

(23) V. H. Dibeler, J. L. Franklin, and R. M. Reese, *J. Amer. Chem. Soc.*, **81**, 68 (1959).

(24) K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957).

(25) Oxidation of amines *via* electron transfer has been shown to involve initial reversible one-electron transfer followed by irreversible steps, thus making the over-all process irreversible; see ref 1.

(26) L. F. Fieser, *J. Amer. Chem. Soc.*, **52**, 5204 (1930).

(27) Adiabatic ionization potentials are needed for this. Adiabatic potentials can be measured by spectroscopy or by photoionization. Vertical ionization potentials obtained by electron impact contain vibrational energy and therefore set an upper limit to the adiabatic values; see ref 3.

(28) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," 1st ed, Academic Press, New York, N. Y., 1966, p 85.

Table II. Data Used in Correlation Equations

Oxidant	Reductant	$E°$, V	IP, V	$\Sigma\sigma^*$	Log k_1, M^{-1} sec^{-1} Exptl	From eq 2	From eq 3
Ferric (1,10-phenanthroline)$_3$ in presence of NO_3^-	Triethylamine	−1.06	7.50	−0.30	6.35	6.12	6.06
Ferric (1,10-phenanthroline)$_3$ in presence of Cl^-	Triethylamine	−1.06	7.50	−0.30	5.99	6.12	6.06
Ferric (5-methyl-1,10-phen)$_3$	Triethylamine	−1.02	7.50	−0.30	5.87	5.80	5.75
Ferric (5,6-dimethyl-1,10-phen)$_3$	Triethylamine	−0.97	7.50	−0.30	5.73	5.41	5.37
Chlorine dioxide	Triethylamine	−0.95	7.50	−0.30	5.09	5.25	5.22
Ferric (4,7-dimethyl-1,10-phen)$_3$	Triethylamine	−0.87	7.50	−0.30	4.82	4.62	4.61
Ferric (3,4,7,8-tetramethyl-1,10-phen)$_3$	Triethylamine	−0.81	7.50	−0.30	4.42	4.15	4.15
Molybdicyanide	Triethylamine	−0.785	7.50	−0.30	3.46	3.96	3.95
Permanganate	Triethylamine	−0.564	7.50	−0.30	1.66	2.23	2.27
Ferricyanide	Triethylamine	−0.47	7.50	−0.30	−1.56		
Chlorine dioxide	Trimethylamine	−0.95	7.82	0.00	4.70	3.51	3.79
Chlorine dioxide	Diethylamine	−0.95	8.01	+0.29	2.74	2.48	2.40
Chlorine dioxide	Diisopropylamine	−0.95	7.73	+0.11	2.22	4.00	3.26
Permanganate	Diethylamine	−0.564	8.01	+0.29	0.15	−0.55	−0.55
Chlorine dioxide	*n*-Butylamine	−0.95	8.71	+0.79	−1.17	−1.13	0.09
Ferric ion	Hydrazine	−0.771	9.00	+1.60	−4.78	−4.30	−5.23
Chlorine dioxide	Benzylamine	−0.95		+1.20	−2.25		−1.95
Permanganate	Trimethylamine	−0.564	7.82	0.00	0.70	0.49	0.84

the hydration energy of an ion. However, because of such effects as dielectric saturation,[29] we do not believe that solvation theory is sufficiently developed to rely on these calculations for a correct oxidation potential. Instead, we tried empirical plots of log k_1 *vs.* $\alpha E° + b\text{IP} + C$ and log k_1 *vs.* $\alpha E° + b\Sigma\sigma^* + C$ for the purpose of demonstrating a rate proportionality to the free energy change of the reversible one-electron transfer step in amine oxidations.

Results

A plot of half-life ($t_{1/2}$) for the oxidation of triethylamine by $K_3Fe(CN)_6$ *vs.* the concentration of added $K_4Fe(CN)_6$ is shown in Figure 1. This plot shows strong retardation by the product $K_4Fe(CN)_6$ and illustrates the reversibility of the rate-determining step.

The influence of the oxidation potential of the oxidant on the rate of oxidation of triethylamine can be summarized in the equation

$$\log k_1 = 11.64E° - 5.78 \qquad (1)$$

with a correlation coefficient of 0.966; the data are given in Table II. More general correlations can be summarized in the form of

$$\log k_1 = -7.84E° - 5.43\text{IP} + 3.85 \qquad (2)$$

(correlation coefficient 0.978) and

$$\log k_1 = -7.64E° - 4.78\Sigma\sigma^* - 3.47 \qquad (3)$$

(correlation coefficient 0.982) data for which are also to be found in Table II. The data for ferricyanide with triethylamine and for chlorine dioxide with benzylamine were not included in calculations of the constants for the equations because these reactions showed abnormal deviations. Possible reasons for these deviations are the following. The oxidation of triethylamine by $K_3Fe(CN)_6$ was so strongly retarded by the $K_4Fe(CN)_6$ product that it was not possible to get an accurate value for the unretarded reaction. The benzylamine–chlorine dioxide reaction has been shown to involve both electron and hydrogen abstraction.[1c] Also, benzylamine does not fall in the plot[3] of amine photoionization potential *vs.* $\Sigma\sigma^*$; this may be caused by the tendency of benzyl compounds to rearrange to form tropylium ions upon ionization.[30] The appearance potential of tropylium ion is lower than normal, apparently because of resonance stabilization.[30]

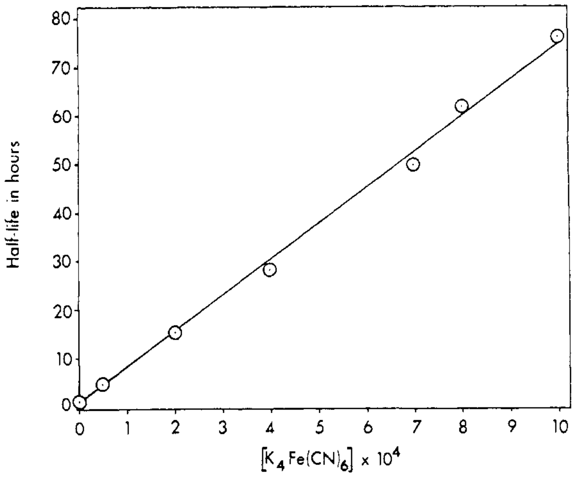

Figure 1. Retardation of oxidation of 0.3 *M* triethylamine by 10^{-4} *M* ferricyanide in borate buffer at pH 8.8.

The oxidation of ethylamine with permanganate was not included in these plots. The predicted values of log k_1, −5.14, using IP = 8.86 V, or −3.37, using $\Sigma\sigma^* = 0.88$, are far from the experimental value[1e] of −0.91. These deviations are probably to be explained by hydrogen abstraction as the main oxidative mechanism, rather than electron abstraction, which is the mechanism described by the present correlations. This is in full agreement with the mechanism found for the permanganate oxidation of benzylamine.[31]

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(29) R. M. Noyes, *J. Amer. Chem. Soc.*, **84**, 513 (1962).

(30) S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *ibid.*, **81**, 2606 (1959).

(31) M. Wei and R. Stewart, *ibid.*, **88**, 1974 (1966).

Discussion

The magnitude of retardation of ferricyanide oxidation[32] of triethylamine by ferrocyanide ($k_2/k_{-1} = 1.3 \times 10^{-5}$) is much larger than the chlorite retardation of chlorine dioxide oxidation of triethylamine ($k_2/k_{-1} = 2.8 \times 10^{-3}$).[1c]

The fact that it is possible to get linear correlations such as eq 2 and 3 suggests that steric effects must be relatively unimportant in amine oxidations *via* a reversible electron transfer mechanism. This is reasonable if it is assumed that the electrons can be transferred through a considerable distance between the reactants, possibly by tunneling.[33] This is the situation of little orbital overlap, which was an assumption of the Marcus theory.

The linearity of the correlation represented by eq 2 also suggests that the solvation energy effects involved in applying the photoionization potential (a gas-phase measurement) to a liquid transition state must be (a) relatively small (unlikely), (b) of constant magnitude, or (c) vary in a linear fashion with the photoionization potential. Correlations with amine pK_a are known to break up into classes, *i.e.*, primary, secondary, and tertiary, most likely because of solvation effects[1g] on hydrogen bonds. Such a phenomenon would be the result of proton transfer and therefore would not necessarily be encountered in electron transfers.

From the foregoing, it may be concluded that the oxidation of aliphatic amines is one among several classes of oxidations whose rates are proportional to the free energy changes ($\Delta F° = -nFE°$) of the rate-determining steps, provided that the reactions in a given class follow the same mechanism. Such linear relationships have been shown both for electron-abstraction reactions[4b] and for oxidation reactions of other types,[34] but there is no reason to assert that all oxidations should exhibit such behavior.

Although there is as yet no theoretical reason to expect thermodynamics (linear free energy relationships) to govern the rate of a chemical reaction[35] when the over-all free energy of the process is considered, we have demonstrated strong evidence for rate proportionality to the free energy changes of rate-determining reversible oxidation–reduction steps.

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[32] In the ferricyanide oxidation of ethylenediaminetetraacetic acid, Lambert and Jones[10b] did not observe retardation by ferrocyanide. Possibly that reaction proceeds by an entirely different mechanism.

[33] See ref 28, p 71.

[34] B. F. Chow, *J. Amer. Chem. Soc.*, 57, 1440 (1935); E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548 (1954).

[35] I. M. Klotz, "Chemical Thermodynamics—Basic Theory and Methods," revised ed, W. A. Benjamin, Inc., New York, N. Y., 1964, p 4.

Kinetics of the Thermal Isomerization of Cyclopropene and 1-Methylcyclopropene

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Abstract: The thermal isomerization of cyclopropene in the vapor phase in the temperature range from 472 to 502°K led to 1-propyne as the only product. At pressures of cyclopropene of 1–3 Torr, and in the presence of an inert gas (carbon dioxide) pressure of 50–60 Torr, the kinetics of the decomposition was homogenous and obeyed the first-order rate equation up to 88% conversion. From the temperature dependence of the reaction at total pressures of ~60 Torr, the first-order rate constant was observed to fit the equation: $k = 10^{12.13}e^{-35200 \pm 1300/RT}$ sec^{-1}. In the absence of a considerable excess of diluent gas, the reaction was not "clean": the kinetics did not follow the first-order rate equation and the rate was greatly influenced by an increase in surface. The thermal decomposition of 1-methylcyclopropene was also studied at reactant pressures of 1–3 Torr and inert gas (carbon dioxide) pressures of 50–60 Torr. In the temperature range from 474 to 499°K the kinetics of the over-all reaction fitted a first-order rate equation, the rate constant being given by the expression: $k = 10^{11.4}e^{-34700 \pm 1200/RT}$ sec^{-1}. The products that were observed were (in the order of decreasing importance) 2-butyne, 1,3-butadiene, and 1,2-butadiene.

The kinetics of the thermal decompositions of strained, small-ring molecules have been extensively studied. Cyclopropene is one of the simplest of such molecules in terms of chemical composition and at the same time perhaps the most strained of the compounds hitherto known,[1] if the strain energy is calculated per carbon atom. We report here data on the thermal decomposition of cyclopropene and 1-methylcyclopropene.

Experimental Section

Cyclopropene and 1-methylcyclopropene were prepared by the Hg($^3P_1$)-sensitized decompositions of furan[2] and 3-methylfuran,[3,4] respectively. The photolyzate, in each case, was passed through a vapor phase chromatograph fitted with a boiling point column to separate the hydrocarbon products from the other material. The mixtures of hydrocarbons were passed through a 7-m column of

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[1] K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, 90, 3395 (1968).

[2] R. Srinivasan, *Pure Appl. Chem.*, 16, 65 (1968).

[3] H. Hiraoka and R. Srinivasan, *J. Am. Chem. Soc.*, 90, 2720 (1968).

[4] H. Hiraoka, submitted for publication.