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.

(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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Contribution from the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598. Received June 9, 1969

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 $\sim$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.

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

Experimental Section

Cyclopropene and 1-methylcyclopropene were prepared by the Hg(^{3}P$_1$)-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

(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.

Table I. Thermal Decomposition of Cyclopropene (Inert Gas: CO₂)

Temp, °K	Cyclopropene, Torr	Total pressure, Torr	Time, sec	% conversion	$k \times 10^4$, sec⁻¹	Remarks
502.6	1.88	46.00	1,275	59.4	7.07	Packed cell
502.6	1.45	44.85	1,900	70.8	6.48	Packed cell
501.8	1.12	59.95	600	32.1	6.44	
501.8	0.99	60.15	900	42.9	6.23	
501.8	1.44	60.80	1,275	63.1	7.83	
501.7	2.54	88.10	1,850	71.5	6.78	
501.8	1.38	60.95	3,050	82.4	5.69	
497.3	1.22	60.05	1,850	63.8	5.50	
497.3	1.19	60.75	2,850	75.8	4.97	
497.5	2.09	60.35	5,520	89.2	4.03	
497.3	1.10	60.25	5,900	90.5	3.99	
494.1	1.00	44.75	1,850	41.1	2.86	Packed cell
494.1	1.04	44.75	3,650	67.4	3.07	Packed cell
493.8	1.19	58.45	440	16.4	4.07	
493.8	1.34	66.45	901	33.4	4.52	
493.8	1.53	60.75	1,270	36.7	3.60	
493.8	1.13	58.85	1,850	45.9	3.32	
493.8	1.23	59.50	1,850	54.5	4.26	
493.8	1.16	59.00	3,450	71.6	3.65	
493.8	1.10	53.15	4,850	78.2	3.14	
493.8	1.12	58.30	5,520	86.8	3.66	
488.2	1.01	57.75	1,850	44.5	3.18	
488.2	0.99	58.95	2,800	57.2	3.03	
488.3	1.08	59.35	6,400	72.8	2.03	
488.3	1.09	59.60	10,000	88.2	2.13	
483.6	1.11	58.15	2,695	34.6	1.58	
483.7	0.97	57.90	3,150	47.7	2.06	
483.6	1.39	77.85	5,000	49.7	1.37	
483.6	1.16	58.05	7,200	77.4	2.07	
483.1	1.10	39.60	2,765	36.4	1.62	Packed cell
483.1	1.07	44.30	3,960	50.9	1.80	Packed cell
477.7	1.23	57.90	4,300	33.1	0.93	
477.7	1.20	57.50	8,250	53.7	0.93	
477.7	1.23	54.65	8,250	53.5	0.93	
477.8	0.71	58.60	10,750	63.2	0.93	
477.7	1.49	58.50	13,300	69.1	0.88	
477.8	0.80	58.70	14,758	81.3	1.14	
477.1	1.31	44.10	3,600	31.8	1.06	Packed cell
477.1	1.51	44.20	7,020	56.0	1.17	Packed cell
471.9	1.32	58.10	3,600	25.9	0.83	
471.9	1.15	57.90	6,450	43.4	0.88	
471.9	1.47	57.70	9,800	58.4	0.89	
471.9	1.31	58.10	17,300	71.0	0.72	
471.9	0.82	58.20	20,900	71.3	0.60	
471.3	1.51	43.55	14,675	62.7	0.67	Packed cell
471.4	1.05	45.90	24,750	78.3	0.62	Packed cell

Figure 1. Plot of the logarithm of the first-order rate constant *vs.* $1/T$ for the thermal decomposition of cyclopropene (inert gas, CO₂): open circles, unpacked cell; filled circles, packed cell.

polyisobutylene to separate the cyclopropenes. These were dried over Drierite, degassed at liquid nitrogen temperature, and stored as gases. Reactant samples were prepared in this way in small lots and used in 2–5 days. No difference in the kinetics was noted from lot to lot.

The cyclopropene usually contained a few per cent of 1-propyne as the only impurity, and this was corrected for in calculating the rate constant. The 1-methylcyclopropene was free from any detectable impurity.

The apparatus that was used has been described.[5] The cell of 120-ml volume was always "conditioned" before use by the pyrolysis of propadiene at 670°K for 20 hr or more.

Analyses were performed on a Perkin-Elmer 154 D vapor fractometer with a 7-m column of polyisobutylene at room temperature.

Results

Since gaseous samples of cyclopropene which were stored in a glass bulb at room temperature seemed to undergo a reaction which led to a diminution in pressure, it was suspected that the polymerization of cyclopropene, which is well known in the condensed phase,[6]

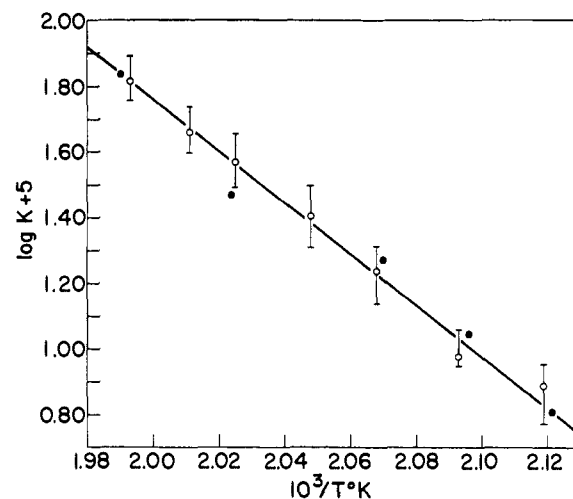(5) R. Srinivasan and A. A. Levi, *J. Am. Chem. Soc.*, **85**, 3363 (1963).

may occur even in the gas phase. In order to minimize this reaction, and to conserve material, the studies reported here were carried out at 1–3 Torr of reactant. It was observed that the first-order rate constants that were obtained under these conditions decreased with increasing conversion and greatly accelerated on increasing the surface-to-volume ratio of the cell, but at the same pressure of cyclopropene, the addition of about 50–60 Torr of CO₂ gave satisfactory kinetic results. All of the data reported here, both for cyclopropene and 1-methylcyclopropene, were carried out only in the presence of a large excess of CO₂.

Kinetic data on the pyrolysis of cyclopropene are given in Table I.

There was no measurable change in the total pressure in the system after various fractions of the material had been pyrolyzed. The pyrolyzed sample condensed completely at liquid nitrogen temperature. Analysis of this material showed only one product, which was identified as propyne on the basis of its infrared spectrum.

The first-order rate constants for the rate of disappearance of cyclopropene were independent of conversion up to 88% conversion. The rate of the reaction was unaffected when the cell was packed with glass tubes which increased the surface-to-volume ratio by a factor of 17. The temperature coefficient of the reaction was the same (within experimental error) in both packed and unpacked cells. Evidently the reaction was truly homogeneous.

A plot of the logarithm of the first-order rate constant *vs.* the reciprocal of the absolute temperature is given in Figure 1. The best straight line through all the points, as determined by least-squares analysis, gave an activation energy of 35,200 ± 1300 kcal/mole and a pre-exponential factor of $10^{12.13}$ sec⁻¹.

Kinetic data on the pyrolysis of 1-methylcyclobutene are given in Table II.

The products of the decomposition in the order of decreasing importance were 2-butyne, 1,3-butadiene, and 1,2-butadiene. There was no net increase in pressure after various fractions of the starting material

(6) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960); see also P. Dowd and A. Gold, *Tetrahedron Letters*, 85 (1969).

Table II. Isomerization of 1-Methylcyclopropene[a]

Temp, °C	No. of runs averaged[b]	Range of conversion	Product composition,[c] %			Rate constant × 10^4 sec^{-1}
			1,3-Butadiene	1,2-Butadiene	2-Butyne	
498.5	10 (6)	18.1–89.0	5.9	2.6	91.5	1.73
490.7	2 (2)	58.6–76.3				1.42
489.7	2 (0)	36.4–64.3	4.8	1.8	93.4	0.812
481.9	4 (2)	22.6–52.1	7.8	3.1	89.6	0.512
474.3	5 (3)	29.2–53.2	3.6	2.3	94.2	0.306

[a] Average pressures of reactant, 1.6 Torr, and CO_2, 41.5 Torr, both at reactant temperature. [b] Runs in packed cells are indicated in parentheses. [c] Refers to unpacked cells only. In a packed cell the ratio of 2-butyne to 1,3-butadiene was consistently smaller.

had been pyrolyzed. The first-order rate constants for the disappearance of 1-methylcyclopropene were constant to 89% conversion. The rate of decomposition and the temperature coefficient for the reaction were the same (within experimental error) in both packed and unpacked cells. Hence, the reaction was homogeneous in character.

A plot of the logarithm of the over-all first-order rate constant vs. the reciprocal of the absolute temperature gave an activation energy of 34,700 ± 1200 kcal/mole and a preexponential factor of $10^{11.4}$ sec^{-1}. The rate data for the formation of each of the products were treated separately in the same way. The activation energies for the formation of 2-butyne, 1,3-butadiene, and 1,2-butadiene were 34.6 ± 0.7, 44.6 ± 2.5, and 39.1 ± 5.6 kcal/mole, respectively. The increase in the uncertainties in these figures reflects the difficulties in the analysis for these products. In separate experiments, it was observed that all three of the products were stable to pyrolysis at the highest temperature used in this work.

It seems appropriate to consider at this point the probable influence of pressure on the activation energies that were determined in this work. From a consideration of the theory of unimolecular reaction rates,[7] it is reasonable to expect that a small molecule such as cyclopropene, with only seven atoms, would be in the "fall-off" region of its pressure–rate constant curve at a pressure of 60 Torr. Experimental difficulties made it impossible to obtain meaningful rate data over a range of pressures. However, it is encouraging that the experimental activation energy for 1-methylcyclopropene is the same (within experimental error) as for cyclopropene. The known fall-off behavior of other C_4 compounds[8] suggests that 1-methylcyclopropene may be within 10% of its high-pressure rate constant at 60 Torr. The fact that much of this pressure is due to CO_2 and not the reactant itself would quality this claim. It seems likely, but by no means conclusive, that the activation energy for cyclopropene at its high-pressure limit would be close to the value determined here.[9]

Discussion

It has already been noted[12] that the thermal decomposition of cyclopropene to propyne (eq 1) is analogous

(7) L. S. Kassel, "Kinetics of Homogenous Gas Reactions," Reinhold Publishing Corp., New York, N. Y., 1932, Chapter Vs and X.
(8) C. Genaux, F. Kern, and W. D. Walters, J. Am. Chem. Soc., 75, 6196 (1953).
(9) There is a further tacit assumption here that the high-pressure activation energy for cyclopropene will not be altered by alkyl substitution. This happens to be the case in cyclopropane[10] and cyclobutane[11] but is merely a guess as far as cyclopropene is concerned.
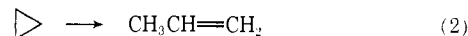(10) J. P. Chesick, J. Am. Chem. Soc., 82, 3277 (1960).
(11) M. N. Das and W. D. Walters, Z. Physik. Chem., (Frankfurt), 15, 22 (1958).
(12) H. M. Frey, Advan. Phys. Org. Chem., 4, 147 (1965).

$$\triangleright \longrightarrow CH_3C \equiv CH \qquad (1)$$
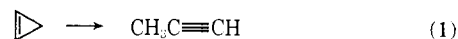
to the thermal decomposition of cyclopropane to propylene (eq 2). Benson and O'Neal[13] have provided a

$$\triangleright \longrightarrow CH_3CH = CH_2 \qquad (2)$$

quantitative analysis of the decomposition of a number of molecules which incorporate a cyclopropane ring. In their view these reactions go through a diradical intermediate (a trimethylene) as follows.

$$\triangleright \underset{2b}{\overset{2a}{\rightleftharpoons}} \cdot CH_2 - CH_2 - CH_2 \cdot \overset{2c}{\longrightarrow} CH_3CH = CH_2$$
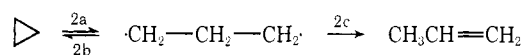
The ring closing (2b) is faster than hydrogen migration from the biradical (2c) by a factor of 22 at 750°K. The application of the same mechanism to cyclopropene (steps 1a, 1b, and 1c) suggests that certain new factors

$$\triangleright \underset{1b}{\overset{1a}{\rightleftharpoons}} \cdot CH = CH - CH_2 \cdot \overset{1c}{\longrightarrow} CH_3C \equiv CH$$
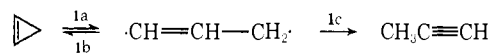
have to be taken into consideration. Those that may affect the activation energy are as follows.

1. The strain energy is greater in cyclopropene as compared to cyclopropane (52.6 vs. 27.5 kcal/mole[1]).

2. The diradical intermediate from cyclopropene can gain some stabilization from the resonance structures: $\cdot CH = CH - CH_2 \cdot$ and $:CH - CH = CH_2$. This would be less than 12 kcal/mole which has been estimated to be the allylic resonance energy in $C_3H_5 \cdot$.[14]

3. The migration of a hydrogen atom has to be from an unsaturated carbon which can be expected to increase the activation energy for step 1c relative to 2c. Since the over-all activation energy $= E_{1a} - E_{1b} + E_{1c}$, it is obvious that the increase in strain energy of 25.1 kcal/mole accounts for a large part of the diminution in E_1 compared to E_2.

There is a decrease of 10^3 in the A factor for cyclopropene relative to the A factor for cyclopropane which is difficult to resolve. An important consideration may be the decreased symmetry in the decomposition pathway.[13] Thus step 2a can occur in one of three equivalent ways and 2c can occur in one of four ways. In cyclopropene, the ring can open in one of only two ways and the hydrogen migration then has no choice. These symmetry considerations will decrease the A factor in the latter instance by $10^{0.78}$ or about 25% of the decrease that is observed. The rest of the decrease can be qualitatively attributed to the increased rigidity in the diradical. It should be emphasized that no evidence for the diradical mechanism in cyclopropenes has been
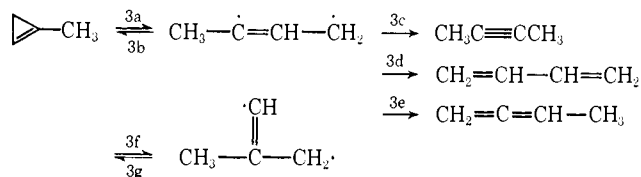
(13) S. W. Benson and H. E. O'Neal, submitted for publication.
(14) D. M. Golden, N. A. Gac, and S. W. Benson, J. Am. Chem. Soc., 91, 2136 (1969).

obtained in this or any other study. It can even be argued that the A factor of less than 10^{13} points to a closed structure for the activated complex.

Thermochemical considerations[1] show that the isomerizations of 1-methylcyclopropene to 2-butyne, 1,3-butadiene, and 1,2-butadiene are exothermic by 23.5, 32.3, and 19.4 kcal/mole, respectively, but this order does not correlate with the importance of the formation of these products in the pyrolysis.

The diradical mechanism can be applied to this system to give the following possibilities.

$$\triangleright\!\!-CH_3 \underset{3b}{\overset{3a}{\rightleftharpoons}} CH_3\!\!-\!\!\dot{C}\!\!=\!\!CH\!\!-\!\!\dot{C}H_2 \overset{3c}{\longrightarrow} CH_3C\!\!\equiv\!\!CCH_3$$

$$\overset{3d}{\longrightarrow} CH_2\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH_2$$

$$\underset{3g}{\overset{3f}{\rightleftharpoons}} \underset{CH_3\!\!-\!\!\overset{\|}{C}\!\!-\!\!CH_2\cdot}{\overset{\cdot CH}{\|}} \overset{3e}{\longrightarrow} CH_2\!\!=\!\!C\!\!=\!\!CH\!\!-\!\!CH_3$$

The diradical that is formed in step 3f has no simple alternative except to return to 1-methylcyclopropene.

All the observed products can be explained by pathways which originate in the linear diradical formed in step 3a. It is interesting that 1,2-butadiene is the only product that can be formed in two distinct ways. One of these involves a 1,4-hydrogen shift over a double bond, while the other requires a 1,2-hydrogen shift across a double bond. Neither process seems sterically simple. Both 2-butyne and 1,3-butadiene are formed by 1,2-hydrogen shifts in the diradical. 1,3-Butadiene is a less important product (than 2-butyne) although its formation requires the migration of one of three equally possible hydrogen atoms in the methyl group in 1-methylcyclopropene. A clear understanding of the stereochemistry of the diradical may serve to explain these peculiarities.

Pyruvate Dimerization Catalyzed by Nickel(II) and Zinc(II). I. Equilibrium with Nickel(II) and Zinc(II)[1]
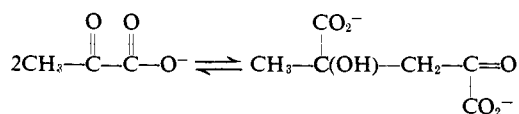
D. E. Tallman and D. L. Leussing

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Abstract: Dimerized pyruvic acid, $HO_2CCOCH_2C(OH)(CH_3)CO_2H$, behaves as a dibasic acid: $pK_{1a} = 1.73$, $pK_{2a} = 3.72$. The dianion forms 1:1 and 2:1 complexes with both Ni(II) (log β_1 1.50, log β_2 2.80) and Zn(II) (log β_1 1.72, log β_2 3.00). The stabilities are of the order observed with bidentate oxygen donors. Comparison with model ligands suggests that the predominant mode of chelation involves the hydroxyl and carboxyl groups attached to the asymmetric carbon.

There has been considerable interest in recent years in the metal ion promotion of nucleophilic organic reactions.[2-5] This interest is partially attributed to the possible relationship of these reactions to analogous enzymatic processes. An understanding of the factors that determine the effectiveness of various metal ions and the mechanisms by which the metal ions function to accelerate a given reaction in these model systems should prove to be a valuable asset for the elucidation of the role of metal ions in metal-ion-activated enzyme systems.

The metal-ion promotion of pyruvate dimerization has been known for many years.[6,7] However, there ap-

pears to be no quantitative information on the kinetics of this reaction or on the nature and stability of the metal complexes of dimeric pyruvate. In order to understand the kinetics of this interesting reaction, it is necessary to have a complete description of the reaction solution in terms of all species present under a given set of conditions. The present investigation was undertaken to determine the acid dissociation constants of monomeric and dimeric pyruvic acid and the stabilities of the various complexes of monomeric and dimeric pyruvate with Ni(II) and Zn(II).

Experimental Section

Dimer-free sodium pyruvate was supplied by the Sigma Chemical Co. and was stored at 0.5^c. Analysis by ion exchange of Na$^+$ for H$^+$ followed by titration with NaOH indicated a purity of 99.6 ± 0.1% calculated as $NaC_3H_3O_3$. Recrystallization from water gave no significant change in purity. Because sodium pyruvate solutions slowly dimerize upon prolonged standing, stock solutions were prepared immediately before use.

Stock solutions of metal chlorides were prepared and standardized according to accepted methods.

Solutions containing pyruvate dimer were prepared immediately before use by adding an aliquot of 0.01 M potassium cyanide solution as catalyst to an aliquot of 1.00 M sodium pyruvate solution and diluting to an accurately known volume after dimerization equilibrium was attained. The time required for the establishment of equilibrium under these conditions was determined spec-

$$2CH_3\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O^- \rightleftharpoons CH_3\!\!-\!\!\underset{CO_2^-}{\overset{CO_2^-}{\underset{|}{\overset{|}{C}(OH)}}}\!\!-\!\!CH_2\!\!-\!\!C\!\!=\!\!O$$

(1) This research has been supported by a grant from the National Science Foundation.

(2) M. Bender, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 19.

(3) M. Jones, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 153.

(4) J. Halpern, *Ann. Rev. Phys. Chem.*, 16, 103 (1965).

(5) J. Halpern, *Chem. Eng. News*, 44 (45), 68 (1966).

(6) L. Wolff, *Ann. Chem.*, 305, 154 (1899).

(7) A. W. K. DeJong, *Rec. Trav. Chim.*, 20, 81 (1901).