may be sensitive to the surface layer on the wall. It is possible that oxygen affects the surface layer and indirectly influences the formation of acetone in its keto structure. A probable mechanism is the oxidation of formaldehyde, which is one of the products, on the wall to give a surface layer which can prevent or slow down the enol to keto reaction. Oxygen can thus influence this photochemical reaction in a way which does not involve the usual routes, *i.e.*, by the trapping of free radicals or by the quenching of triplet states.[15]

If this explanation is correct, it cannot be applicable to the case of 2-pentanone in which *both* acetone and ethylene formation decreased on the addition of oxygen.[13] It should be interesting to see if oxygen is effective as a quencher in that system even at an elevated temperature.

NOTE ADDED IN PROOF.—Borkowski and Ausloos (*J. Phys. Chem.*, **65**, 2257 (1961), have shown that oxygen is an effective quencher of the type II process at 305°K. as well as at 420°K. in the photolysis of 2-pentanone-4,5,5-$d_3$ at 3130 Å.

**Acknowledgment.**—The author wishes to thank Dr. Harold L. Friedman for his advice and encouragement during the course of this work.

[15] It has been pointed out by one of the referees that if the scavenging effect of oxygen on free radicals in this system is not complete, other mechanisms may also be devised to account for the observed products. The formation of acetone may be by the reaction

$$CH_3COCH_2\cdot + CH_3O\cdot \rightarrow CH_3COCH_3 + CH_2O$$

if the primary process is

$$CH_3COCH_2OCH_3 + H\nu \rightarrow CH_3COCH_2\cdot + CH_3O\cdot.$$

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY, STANFORD, CALIFORNIA, AND THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA, AND LOS ANGELES, CALIFORNIA]

# Kinetics of the Thermal Decomposition of Nitric Acid Vapor. IV. A Shock Tube Study Between 800–1200°K.

BY HALSTEAD HARRISON,[1] H. S. JOHNSTON AND E. R. HARDWICK

RECEIVED OCTOBER 26, 1961

The decomposition of nitric acid vapor in excess argon was studied in a shock tube between 800 and 1200°K. The reaction was followed in terms of the appearance of nitrogen dioxide and of the appearance and disappearance of the intermediate, $NO_3$. At total concentrations near $10^{-5}$ mole/cc. the decomposition is controlled by the unimolecular reaction

$$M + HNO_3 \xrightarrow{a} HO + NO_2 + M$$

near its second order limit, with

$$\log a = (15.2 \pm 1.0) - \frac{30.6 \pm 1.8}{2.303\,R} \cdot \frac{1000}{T}\ (\text{mole/cc.})^{-1}\ \text{sec.}^{-1}$$

The presence in this system of $NO_3$ and its rate of disappearance are consistent with previous work on the decomposition kinetics of nitric acid and nitrogen pentoxide.

## Introduction

The decomposition of nitric acid vapor has previously been studied between 500 and 700°K. in conventional systems and at slow rates.[2] The reaction was found to involve a complex, non-chain mechanism

$$M + HNO_3 \underset{a_{-1}}{\overset{a}{\rightleftarrows}} HO + NO_2 + M$$

$$HO + HNO_3 \xrightarrow{j} H_2O + NO_3$$

$$NO_3 + NO_2 \xrightarrow{e} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{f} 2NO_2$$

$$NO_3 + NO_3 \xrightarrow{g} 2NO_2 + O_2$$

The unimolecular decomposition was essentially second order at pressures below 10 mm., and rate $j$ was fast compared to $a_{-1}$. At one atmosphere the reaction was in its complicated intermediate zone between second and first order kinetics, and rates $j$ and $a_{-1}$ were approximately equal. The free radical, $NO_3$, was not observed, but its presence was inferred from kinetic behavior.

Much is known of $NO_3$ from work by Schott and Davidson,[3] who studied the decomposition of $N_2O_5$ in a shock tube between 500 and 1200°K. Their efforts, combined with extensive previous work at lower temperatures, give separately evaluated elementary rate constants for steps $e$ through $g$. Above 1000°K., Schott and Davidson noted in addition the onset of a unimolecular decomposition of $NO_3$ with an activation energy of about 50 kcal./mole, presumably

$$M + NO_3 \xrightarrow{k} NO_2 + O + M$$

The rapid reaction of oxygen atoms with $NO_2$ is known,[4] as is the decomposition of nitrogen dioxide[5]

$$O + NO_2 \xrightarrow{m} NO + O_2$$

$$NO_2 + NO_2 \xrightarrow{l} 2NO_2 + O_2$$

This large body of quantitative data of elementary reactions goes a long way toward predicting

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[1] Chemistry Departmenu, University of Michigan, Ann Arbor, Michigan.

[2] H. S. Johnston, L. Foering and J. R. White, *J. Am. Chem. Soc.*, **77**, 4208 (1955), and references cited therein.

[3] G. Schott and N. Davidson, *ibid.*, **80**, 1841 (1958), and references cited therein.

[4] W. W. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1156 (1957).

[5] R. Huffman and N. Davidson, *J. Am. Chem. Soc.*, **81**, 2311 (1959).

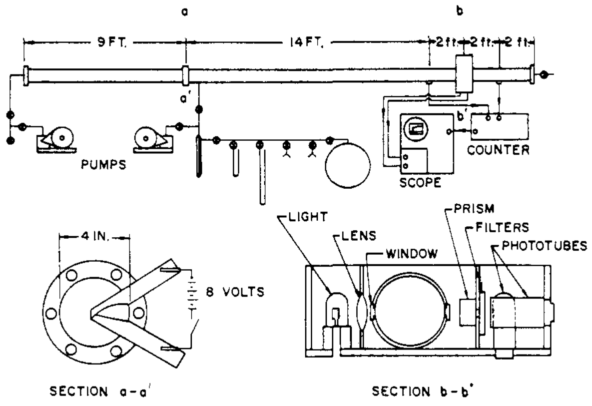

Fig. 1.—Schematic diagram of apparatus.

the behavior of nitric acid vapor at high temperatures. A crucial test of a mechanism dependent upon these reactions is the appearance and disappearance of the $NO_3$ radical over times of about $10^{-4}$ seconds at temperatures near 1000°K. We have carried out such a study.[6] Simultaneous optical examination was made for $NO_2$ and $NO_3$, and net rate constants were obtained for the primary reaction, *a*.

## Experimental

**Reagents.**—Nitric acid was prepared by vacuum distillation of a saturated solution of reagent grades of $KNO_3$ in 96% $H_2SO_4$, between plus and minus 40°. The colorless product could be kept indefinitely at $-78°$ without evidence of decomposition. Nitrogen pentoxide was obtained by reacting an ozonized oxygen stream with $NO_2$. The white, fluffy, crystalline product was trapped out of a colorless gas stream at $-78°$ and could also be stored indefinitely at this temperature. Argon and helium were from commercial cylinders. "Halocarbon" stopcock grease was used on all ground joints.

**Apparatus.**—The aluminum-pipe shock tube was 29 feet long by 4-$^1/_2$" o.d. by 4" i.d. divided into a 20 foot low pressure channel and a 9 foot driver chamber (Fig. 1). The two sections were separated by a double-layered diaphragm of "Mylar" film, usually of 2 or 3 mil thickness, held between bolted flanges. When the channel was filled to a few centimeters pressure and the driver chamber to 2–4 atm., the stressed diaphragm was ruptured by electrically heating a V-shaped aluminum foil placed between its two layers (Fig. 1, sec. a-a'). Two Pyrex windows of $^3/_8$" diameter were mounted on opposite sides of the tube, four feet from the butt plate of the channel (Fig. 1, sec. b-b'). Light from a 12 volt d.c. 48 watt sports car lamp was rendered parallel by a short focal length lens, passed through the shock tube without further collimation than that supplied by the Pyrex windows, and split by a prism into two beams. One of the resulting light beams then passed through a filter pack (Bausch and Lomb 42-47-59 plus Corning No. 3389) having a peak transmittance of 38% at 6400 Å. and a half-peak band width of 200 Å. and was directed to the cathode of a Dumont type 6911 photomultiplier. The second beam traversed another filter pack (B. and L. 33-78-36 plus 1.6 mm. of a saturated $CuSO_4$ solution) having a peak transmittance of 35% at 3680 Å. and a band width of 180 Å. to excite a R.C.A. 1P28 photomultiplier. Signals from the two phototubes were presented on a Tektronix 535 oscilloscope through its dual trace preamplifier, so that transmissions at the two wave lengths could be recorded simultaneously. The time interval between the arrival of the incident shock at two glow discharge triggers[7] located symmetrically 2' on either side of the observation station was presented on an electronic counter to permit calculation of the incident shock mach number. Since the oscilloscope delayed its presentation a controlled time after receiving its trigger pulse from the opening gate of the counter, the arrival time of the shock seen on the photographed trace gave a third interval with which the constancy of the shock velocity could be checked.

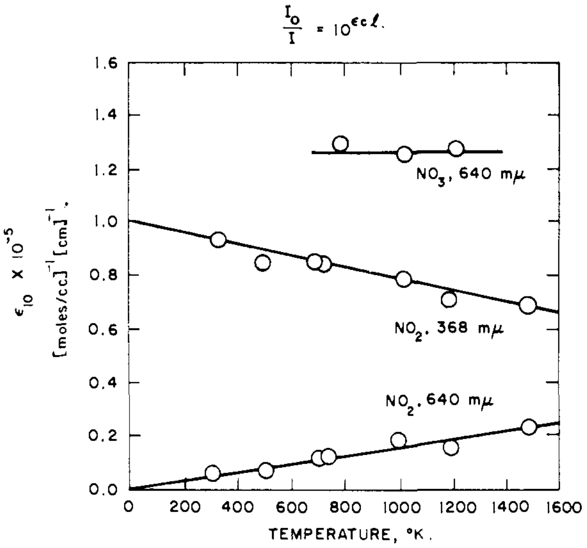

Fig. 2.—Extinction coefficients.

**Procedure.**—In a typical shot, the reactant was vaporized into a 22 liter Pyrex bulb in amounts measured by the pressure reading of a di-*n*-butyl phthalate manometer and by weight loss from a storage vial. Argon was then added and the total pressure measured over a mercury manometer separated from the mixing bulb by an argon-filled diffusion tube. The bulb was then isolated and stirred for 15 min. by a magnetically driven, glass encased, 6 cm. bob, rotating at 3000 r.p.m. After introduction into the evacuated channel of the shock tube, the gas mixture was allowed to equilibrate to tube temperature for five minutes while the light transmissivity of the unshocked gas was checked and the currents through the two glow discharge triggers matched. The tube was then fired, the scope transient recorded with a Dumont polaroid camera, and the incident shock velocity calculated from the display on the electronic timer. From the density and temperature before the shock, the shock velocity and a perfect-gas equation of state, the density and temperature of the shocked gas mixture was then calculated using the classic Rankine–Hugoniot conditions for perfect, one-dimensional flow.[6]

## Results

By the foregoing procedures extinction coefficients of $NO_2$ at the two wave lengths and of $NO_3$ at 640 mμ were measured as functions of temperature by scanning shocked $NO_2$ and, in separate experiments, the equimolar mixture of $NO_2$ and $NO_3$ produced by shocked $N_2O_5$. With these known extinction coefficients (Fig. 2) a series of shots of decomposing $HNO_3$ revealed small but measurable amounts of $NO_3$ between 900 and 1100° K. (Fig. 3a and Table I). Some displays when corrected for the interference of $NO_2$ show a maxi-

TABLE I

$NO_3$ CONCENTRATIONS AND RATES OF DECAY WHEN $[NO_2] = [HNO_3] = [C]$ moles/cc.$^{-1}$

| Shot no. | Mole fraction $HNO_3$ | $<T_2°>$ | Log [C] | Log $[NO_3]$ | Log $\left[-\frac{d \ln [NO_3]}{dt}\right]$ |
|---|---|---|---|---|---|
| 128 | 0.075 | 920 | −6.64 | −7.8 | 2.6 sec.$^{-1}$ |
| 116 | .046 | 1020 | −7.00 | −8.2 | 3.2 |
| 129 | .086 | 1050 | −6.49 | −8.0 | 3.3 |
| 118 | .162 | 1050 | −6.39 | −8.0 | .. |
| 127 | .113 | 1070 | −6.48 | −7.9 | 3.6 |
| 126 | .155 | 1100 | −6.44 | −7.8 | 4.0 |

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(6) For details see: H. Harrison, Stanford University Dissertation (1960), University Microfilms, Ann Arbor, Michigan.

(7) H. Harrison, *Rev. Sci. Instr.*, **29**, 175 (1958).

TABLE II

PRIMARY DATA FOR THE SHOTS OF THIS STUDY

| Shot no. | Shock velocity (cm./sec.) × $10^{-5}$ | $\rho_1$ (mole/cc.) × $10^5$ | $X$ (mole fraction of $HNO_3$) | $\rho_1/\rho_2$ | $T_2/T_1$ | Log [M] (mole/cc.) | Log $\frac{k_{uni}}{[M]}$ (sec.)$^{-1}$ (mole/cc.)$^{-1}$ | $\frac{1000}{T_2}$ |
|---|---|---|---|---|---|---|---|---|
| 133 | 1.008 | 0.321 | 0.0268 | 0.319 | 3.91 | −5.00 | 9.42 | 0.861 |
| 132 | 0.982 | .321 | .0288 | .329 | 3.81 | −5.01 | 9.23 | .889 |
| 142 | .964 | .337 | .0254 | .328 | 3.68 | −4.99 | 9.15 | .923 |
| 141 | .935 | .321 | .0267 | .333 | 3.50 | −5.02 | 9.07 | .962 |
| 156 | .938 | .450 | .0388 | .330 | 3.53 | −4.87 | 8.63 | .977 |
| 149 | .922 | .200 | .0388 | .333 | 3.44 | −4.92 | 8.57 | .991 |
| 151 | .910 | .244 | .0388 | .338 | 3.29 | −5.12 | 8.23 | 1.041 |
| 139 | .885 | .348 | .0291 | .343 | 3.23 | −4.99 | 7.82 | 1.048 |
| 152 | .887 | .161 | .0388 | .340 | 3.24 | −5.33 | 8.25 | 1.049 |
| 143 | .848 | .337 | .0267 | .352 | 3.08 | −5.02 | 7.96 | 1.095 |
| 134 | .832 | .545 | .0252 | .357 | 2.95 | −4.87 | 7.63 | 1.133 |
| 150 | .831 | .244 | .0388 | .354 | 2.96 | −5.16 | 7.60 | 1.136 |
| 153 | .822 | .440 | .0388 | .355 | 2.80 | −4.90 | 7.32 | 1.194 |
| 157 | .799 | .413 | .0226 | .366 | 2.79 | −5.01 | 7.18 | 1.197 |
| 148 | .778 | .385 | .0288 | .372 | 2.68 | −4.99 | 7.14 | 1.242 |

mum in $NO_3$ concentration; others reveal only a decreasing trace. All have been characterized in Table I by the concentrations and rates of disappearance when the nitric acid is half decomposed.

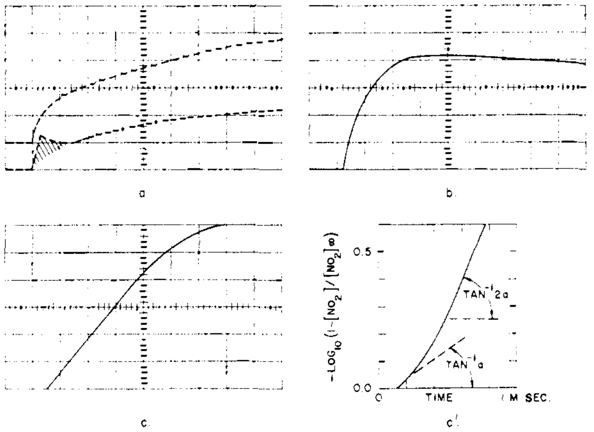

Fig. 3.—Oscilloscope displays: a. Dual trace showing transmissions at 1050°K., the shaded area is $NO_3$. Vertical scale: upper trace (368 mμ), 20% transmission/cm.; lower trace (640 mμ), 10% transmission/cm. Horizontal scale: 50 μsec./cm. b. Appearance and decay of $NO_2$ (368 mμ) at 1160°K. Vertical scale: 8.33% transmission/cm. Horizontal scale: 20 μsec./cm. c. Appearance of $NO_2$ (368 mμ) at 880°K. Vertical scale: 8.33% transmission/cm. Horizontal scale: 100 μsec./cm. c'. First order rate plot of shot c.

In the shocked nitric acid mixtures reported in Table I, the large mole fractions of reactant used, though necessary to obtain confident identification of $NO_3$, had the unfortunate effect of producing correspondingly large temperature drops due to the endothermic reaction. To monitor carefully the rate of nitrogen dioxide's appearance, the mole fractions of nitric acid vapor were therefore reduced so that maximum temperature corrections were less than 30°K. Three separate procedures were then used to evaluate the first order rate constants for the appearance of $NO_2$:

(1) At the very highest temperatures it was possible to measure an extinction coefficient for each shot by observing the transmission when essentially all of the $HNO_3$ was pyrolyzed. For these shots a standard first order plot was made, from whose slope a rate constant could be calculated. Ordinarily these curves were straight, but shots made on the more rich mixtures gave a slight negative curvature, a situation to be expected if self-cooling from the endothermic reaction is appreciable. For these curved plots the initial slopes were measured, and the rates shown to agree with the average slopes at a temperature and density estimated by a linear correction for the extent of reaction.

(2) At somewhat lower temperatures (*ca.* 1050°K.) it was no longer possible to estimate the extinction at infinite time directly from the large-time values on the recorded oscilloscope traces. However, for a first order reaction one may still obtain a rate constant from the curvature of a transmission–time plot without foreknowledge of the extinction coefficient. Here, the log of the time derivative of the optical density was plotted with respect to time, and a rate constant was taken from the slope. The value of the constant so measured always agreed within a factor of 1.5 with that determined by method 1, using an extinction coefficient taken from Fig. 2. We take the agreement of the two methods as evidence that the reaction is still first order at these intermediate temperatures but prefer to report the values obtained by the internal method.

(3) Finally, at the lowest temperatures (less than 950°K.) the oscilloscope traces show only a rising straight line. Rate constants for these low-temperature shorts were calculated with the aid of Fig. 2 and reported in Table II as if first order.

## Discussion

The discovery of $NO_3$ in decomposing nitric acid vapor is a cardinal result of this study. The identification rests on a time dependent extinction at 640 mμ in excess of that due to interfering $NO_2$, corroborated by a measured concentration and rate of disappearance consistent with a steady-state calculation.[6] Though $NO_3$ certainly does not disappear by a single, elementary process, it is in-

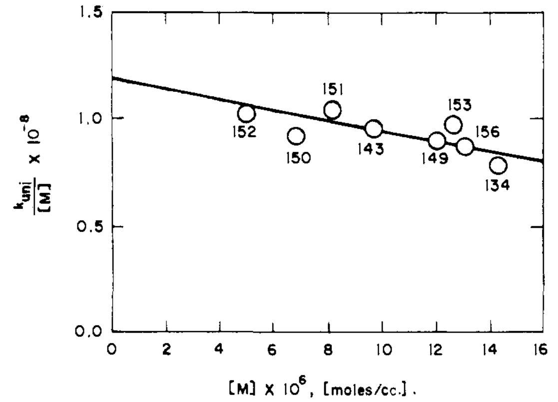

Fig. 4.—Test of kinetic order with respect to total concentration.

teresting that an Arrhenius-like plot of log $-\frac{d\ln[NO_3]}{dt}$, measured at the time when $[HNO_3] = [NO_2]$, shows a large slope ($E_{act} \sim$ 40–50 kcal.) which is perhaps increasing with temperature, an observation which supports Schott and Davidson's conjecture that at temperatures above 1000°K. the process $M + HNO_3 \xrightarrow{k} NO_2 + O + M$ may become important.[2] We hesitate to overinterpret our information about rates involving $NO_3$, however, for the very large subtractive corrections for interference by $NO_2$ give correspondingly large uncertainties.

That the rate of appearance of $NO_2$ is approximately proportional to the first power of the total concentration is shown by the small slope of a plot of $k_{uni}/[M]$ *vs.* [M] for selected points corrected to the mean of their reciprocal temperatures, 1/915°K. (Fig. 4). The over-all reaction thus behaves as if governed by a unimolecular decomposition near its low concentration, second order limit, and does so, interestingly, at concentrations several times higher than those for which this behavior is observed at 650°K.[2] The appropriate Arrhenius plot is then of $k_{uni}/[M]$ against $1000/T$ (Fig. 5).[8] Here, a fit of a straight line through our experimental points using least-square's statistics with the precision of neither of the coördinates considered to be greater than the other gives

$$\log \frac{k_{uni}}{[M]} = (15.2 \pm 1.0) - \frac{30.6 \pm 1.8}{2.303R} \cdot \frac{1000}{T}$$

Two considerations complicate a direct comparison of these data with that of earlier studies where measurements were largely made with pure nitric acid vapor and under conditions such that the Bodenstein approximation, $d[NO_3]/dt = 0$ was applicable. Under these conditions Johnston, Foering and White[2] found

$$\log(2a) = 17.0 - \frac{38.3 \pm 1.4}{2.303R}\frac{1000}{T}$$

In the present study measurements were made with an excess of argon and under conditions such that the steady-state approximation is certainly not applicable, at least when applied to $NO_3$ in the estimation of initial rates. We therefore identify the initial, high-temperature values of $k_{uni}/[M]$ with $a$. rather than $2a$, and note with interest that in the low-temperature shots of this study (Fig. 3c′) the autocatalytic effect of $NO_3$ ultimately doubles the initial rate.

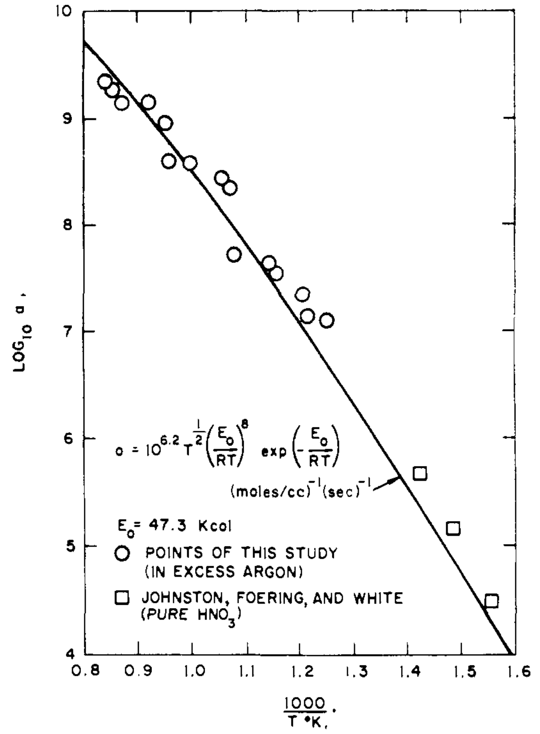

Fig. 5.—Arrhenius plot for the reaction $M + HNO_3 \xrightarrow{a} HO + NO_2 + M$.

In the classical form of the Rice–Ramsperger–Kassel formulation of reaction rates, a unimolecular decomposition near its low-pressure, second-order limit may have an activation energy which is less than the energy of molecular cleavage by $\sim(s - 3/2)RT$, where $s$ is the number of "square terms" in the internal motions of a molecule which may store energy for its rupture.[9] With $E_0$ for the present reaction taken to be 47.3 kcal./mole,[10] our data taken at a mean effective temperature of 955°K. would require $s$ to be 10.3 ± 0.9, while that of Johnston, Foering and White at 672°K. require $s$ to be 8.2 ± 0.7. Together, the high and low temperature studies suggest

$$a = 10^{6.2}\,T^{1/2}\left(\frac{E_0}{RT}\right)^{8.0} e^{-\frac{E_0}{RT}}\ [\text{mole/cc.}]^{-1}[\text{sec.}]^{-1}$$

with

$$E_0 = 47.3 \text{ kcal./mole}$$

as a reasonable fit for both sets of data between 650 and 1200°K. (Fig. 5). Again, an imperfectly known, and possibly temperature-dependent, factor accounting for the relative collision efficiencies

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(8) There is an element of circularity in the preceding analysis, for the plot of Fig. 4 depends in part upon a temperature correction obtained from Fig. 5. The question is really moot, however, for the latter plot is heavily weighted by points having concentrations near $10^{-5}$ mole/cc., and in consequence the activation energy is not critically dependent upon whether $k_{uni}$ or $k_{uni}/[M]$ is plotted against $1000/T$.

(9) See, for example, R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," The University Press, Cambridge, 1939.

(10) $\Delta E_0{}^0$ was derived from data in: W. Giauque and W. Forsythe, *J. Am. Chem. Soc.*, **64**, 48 (1942), R. Barrow and A. Downie, *Proc. Phys. Soc.* (*London*), **A69**, 178 (1956), and "Selected Values of Chemical Thermodynamic Properties," U. S. Bureau of Standards, Circular 500 (1952).

of argon and nitric acid separates the two bodies of data. At 600°K., nitric acid appears to be at least twice as effective an energy transfer agent as argon and was so accounted in fitting the data to the above equation. In Fig. 5, however, the points of both studies are shown without correction for the relative collision efficiencies of the two "M" gases.

If we wish to consider the $s$-parameter to be more than a number imposed upon the data to enforce a fit with theory and if we then identify the number of "square terms" with the internal motions of the nitric acid molecule, it is to be objected that infrared spectra[11] show that for only five of the nine vibrational modes is $h\gamma/kT$ less than or on the order of unity, a rather strict requirement for the classical RRK model. Thus even a generous model is hard put to account for the observed "low" activation energy.

**Acknowledgment.**—This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, Contract AF-49-(638)-306.

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[11] H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Soc. IV*, 4272 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH AND THE UNIVERSITY OF ARIZONA]

# Destructive Autoxidation of Metal Chelates. II. Further Studies of the Effect of Ligand Structure on Initial Rate[1]

BY E. M. ARNETT,[2] H. FREISER AND M. A. MENDELSOHN

RECEIVED DECEMBER 21, 1961

Further results are presented for the destructive autoxidation of iron(III) beta-diketone chelates by molecular oxygen in diphenyl ether as solvent. The new data refute our earlier conclusion that attack occurs on the hydrogen attached to the 3-carbon. Kinetic results indicate that the the reaction does not proceed through a classical radical-chain mechanism and that not all metal acetylacetonates follow the same mechanism. Evidence is presented supporting the supposition that the diacetyl which is always formed in good quantity in the reaction cannot come from the coupling of kinetically free acetyl radicals.

In a previous paper[3] in this series we described the irreversible decomposition of a number of beta diketone chelates under attack by molecular oxygen at 100° in diphenyl ether as solvent. Comparison of the acetylacetonates of fourteen metals showed that only those of metals capable of facile oxidation–reduction underwent reaction at an easily measurable rate.

The structure of the ligand was also varied in order to cast light on the position of initial attack on the chelate molecule. By means of blocking various positions in the organic part of the molecule, it was observed that the replacement of the lone hydrogen on the 3-position of the ligand with phenyl or benzyl groups led to an inert chelate and that replacement of the two methyl groups flanking this hydrogen with large *t*-butyl groups also stabilized the chelate. From these indications it was concluded that the 3-hydrogen was the point of attack, perhaps through some variant of a classical metal-catalyzed chain reaction involving, for example, abstraction of the hydrogen by a peroxy radical.

In the present paper we shall present more observations on metal chelates of other substituted acetylacetonates. In two other papers to follow we shall present extensive new evidence which refutes our original suggestion that the reaction proceeds through a complex chain mechanism. Instead it will be seen that the reaction probably goes by a rather simple mechanism which is consistent with a large body of evidence.

## Results and Discussion

We have focused our main interest on iron(III) chelates and have aimed in particular toward elucidating the mechanism of autoxidation of iron(III) acetylacetonate. There is evidence that not all of the chelates to be discussed follow the same mechanism as does this compound, but because it is convenient for study and might be considered in many ways to be typical, it will be considered as the reference compound. Accordingly, we have chosen to compare the influence of ligands on the reaction mainly through their iron(III) chelates. These are presented in Table I.

TABLE I

RELATIVE INITIAL RATES[3] OF OXYGEN UPTAKE FOR IRON(III) CHELATES

| Ligand | Relative rate |
|---|---|
| Dibenzoylmethane | 7.60 |
| Benzoylacetone | 1.70 |
| 3-Methylacetylacetone | 1.07 |
| Acetylacetone | 1.00 |
| Acetylacetone-3d | 0.98 |
| Dipivaloylmethane | Very slow |
| 3-Phenylacetylacetone | Very slow |
| 3-Benzylacetylacetone | Very slow |

**Iron(III) 3-Methylacetylacetonate.**—The first clear evidence that the 3-position is probably not involved directly in a rate-controlling step was provided by the rapid autoxidation of this chelate. Although the 3-phenyl and 3-benzyl compounds are inert, the 3-methyl compound reacts even faster than the unsubstituted reference compound. In order to test the possibility that the 3-methyl chelate is not following a different mechanistic path than the other iron(III) chelates in Table I,

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[1] From the thesis of M. A. Mendelsohn submitted to the Department of Chemistry of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. Degree, 1960.

[2] Department of Chemistry, University of Pittsburgh, Pittsburgh 13, Pennsylvania.

[3] M. Mendelsohn, E. M. Arnett and H. Freiser, *J. Phys. Chem.*, **64**, 660 (1960).