that the upper curves in this figure are horizontal shows that added salts which act only as strong electrolytes, have very little, if any effect on the yield of hydrazine.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

Kinetics of the Oxidation of Cyclohexane with Nitrogen Pentoxide[1]

BY J. C. D. BRAND[2]

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The kinetics of oxidation of cyclohexane by nitrogen pentoxide have been measured in carbon tetrachloride solution at 0 and 20°. The results are interpreted by a mechanism in which the initial attack on the hydrocarbon is by an NO_3 radical generated by dissociation of the nitrogen pentoxide, $N_2O_5 \rightleftarrows NO_2 + NO_3$, $RH + NO_3 = R\cdot + HNO_3$. The main products of the oxidation, nitrocyclohexane and cyclohexyl nitrate, are formed in bimolecular, parallel reactions of the cyclohexyl radical with nitrogen dioxide; cyclohexyl nitrite is a transient intermediate in the formation of cyclohexyl nitrate. The retardation of the reaction by nitrogen dioxide is analyzed. Induced oxidation of the solvent occurs by a mechanism analogous to radical transfer in polymerization. Relative velocity coefficients of the reactions in the assumed mechanism are calculated from the experimental results. Single-step velocity coefficients are evaluated on the assumption that certain key reactions have the same rate (and activation energy) in solution as at high pressure in the homogeneous gas phase.

The reaction of nitrogen pentoxide with saturated hydrocarbons has recently been examined in its qualitative aspects by Titov and Schitov[3] who observed that the primary oxidation products were the mononitro compound and the nitrate ester of the corresponding alcohol.

$$RH \xrightarrow{N_2O_5} RNO_2 \text{ and } RONO_2$$

This behavior was established for *n*-heptane, *n*-octane and cyclohexane. Oxidation of the *n*-alkanes occurred principally at the methylene group adjacent to the terminal methyl group.

The present study is concerned with the kinetics and mechanism of the oxidation, cyclohexane being chosen for quantitative measurements because of the equivalence of the methylene groups. The results are of interest for two reasons: firstly because the reaction serves as a useful model for the familiar vapor phase nitration process[4] and can be studied under much simpler experimental conditions; and secondly because the participation of a saturated hydrocarbon in a fast reaction at room temperature is arresting and merits examination for its own sake. The measurements in this paper refer to oxidation in carbon tetrachloride solution; the reaction is initially more rapid than the spontaneous decomposition of nitrogen pentoxide[5] but is powerfully retarded by the accumulation of nitrogen tetroxide as the oxidation proceeds. The mechanism involves consecutive, non-chain radical reactions, and radical transfer with the solvent occurs.

Experimental

Materials.—Cyclohexane was submitted to acid extraction and partial freezing, and was twice fractionated in a 60-plate Podbielniak column with a take-off ratio of 1:50. The final product had f.p. 6.60° (*cf.* 6.68 ± 0.05° extrapolated for pure cyclohexane by Aston, Szasz and Fink[6]).

C.P. carbon tetrachloride was purified by treatment with Hg and by extraction with concd. H_2SO_4 and concd. KOH; it was deaerated by refluxing in a current of nitrogen, and freshly distilled from P_2O_5 before use.

Nitrogen pentoxide was prepared from nitrogen dioxide (Matheson) and excess ozone.[7] The crystals were purified by sublimation twice from P_2O_5 in a stream of ozone.

Cyclohexyl nitrate (*cf.*[3,8]) was obtained by esterification of cyclohexanol with nitric acid in 85% sulfuric acid at −5°; b.p. 76° (12 mm.), after washing with 85% phosphoric acid. Cyclohexyl nitrite was prepared by the method of Hunter and Marriott.[9]

Velocity Measurements.—All experiments were conducted in a medium of carbon tetrachloride. Oxygen, which interfered with the course of the reaction, was swept out of the apparatus with a current of dry nitrogen after the final sublimation of the nitrogen pentoxide; the dissolution of the pentoxide in carbon tetrachloride and the subsequent manipulation of the solution was conducted under nitrogen in a closed apparatus. Commencement of the reaction was timed from the addition of cyclohexane. Velocity measurements were made at 0 and 20°.

To follow the reaction, aliquot samples were withdrawn by automatic pipet and were delivered into a measured volume of dilute sodium carbonate solution. After shaking, the aqueous phase (*p*H 9–10) was analyzed for nitrite and chloride and the carbon tetrachloride layer was separated, dried (Na_2SO_4) and examined by infrared methods. The nitrite (from N_2O_4) present in the aqueous phase was estimated with ceric sulfate; the chloride, formed by hydrolysis of phosgene generated by induced oxidation of the solvent, was analyzed by the Volhard method. Nitrogen pentoxide was estimated by delivery of the solution in carbon tetrachloride into acetone containing a few per cent. of water, the nitric acid liberated being titrated potentiometrically with alkali; when present, nitrogen tetroxide contributed to the total nitric acid and was determined by a simultaneous analysis for nitrite by the previous procedure. In the potentiometric titration nitric acid was estimated independently of nitrous acid which, in the acetone medium, was very weakly acidic.

Infrared Spectra.—The infrared spectra confirmed that the major products of the reaction were nitrocyclohexane and cyclohexyl nitrate, as reported by Titov and Schitov.[3] The most prominent bands of these two absorbers in CCl_4 solution were at: nitrocyclohexane, 6.44 and 7.26 μ; cyclohexyl nitrate, 6.11, 7.84 and 11.55 μ. Relatively smaller amounts of chlorocyclohexane and trichloronitromethane were identified by the following bands (excluding bands unresolved from bands of unreacted cyclohexane, or obscured by solvent absorption): for $C_6H_{11}Cl$, 7.89, 8.24, 10.06, 11.25 and 14.60 μ; for CCl_3NO_2, 6.19, 7.41, 7.65, 11.10, 11.61, 11.88 and 14.93 μ. These bands were clearly seen if the major reaction products were first removed from

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[1] This research was supported by the United States Air Force under Contract No. AF 33(038)-23976 monitored by the Office of Scientific Research. Report Control Number OSR-TN-54-19.

[2] The University, Glasgow W. 2, Scotland.

[3] A. I. Titov and N. V. Schitov, *Doklady Akad. Nauk*, **81**, 1085 (1951).

[4] G. B. Bachman, L. Addison, J. V. Hewett, L. Kohn and A. Millikan, *J. Org. Chem.*, **17**, 906 (1952).

[5] H. Eyring and F. Daniels, THIS JOURNAL, **52**, 1472 (1930).

[6] J. G. Aston, G. J. Szasz and H. L. Fink, *ibid.*, **65**, 435 (1943).

[7] J. H. Smith and F. Daniels, *ibid.*, **69**, 1735 (1947).

[8] Fr. Fichter and A. Petrovich, *Helv. Chim. Acta*, **24**, 256 (1941).

[9] L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 285 (1936).

the solution by extraction with sulfuric acid. The molar ratio

$$[C_6H_{11}Cl]/[CCl_3NO_2] = 2.5 \pm 0.7 \qquad (1)$$

was calculated from the intensities of the bands at 14.60 and 14.92 μ. Within the rather wide limits of error, due mainly to the intrinsic weakness of the chlorocyclohexane spectrum, this ratio showed no observable trend with the kinetic conditions.

Absorption at 6.04 μ indicated a further oxidation product which most probably absorbed also in the region of the 7.84 and 11.55 μ bands of cyclohexyl nitrate as, relative to the 6.11 μ band, these two bands were appreciably more intense in the spectrum of the reaction products than in the reference spectrum of cyclohexyl nitrate. This suggests that the 6.04 μ band marks a compound containing the nitrate ester function, but attempts to identify it more closely were unsuccessful. The intensity of the 6.04 μ band was approximately a constant fraction of the cyclohexyl nitrate absorption at 6.11 μ, and presumably the slow steps in the formation of these two compounds are the same.

If oxygen was admitted to the reaction, an additional pair of bands (5.87 and 7.75 μ) appeared in the product spectrum, suggesting a new absorber containing the $-ONO_2$ group. This compound had peroxidic properties and was reduced with aqueous $FeSO_4$ or KI; on standing it decomposed slowly in solution forming phosgene and some cyclohexanone. Possibly this substance is cyclohexyl pernitrate, formed by the steps

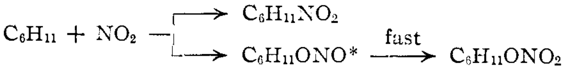
$$C_6H_{11}\cdot \xrightarrow{O_2} C_6H_{11}OO\cdot \xrightarrow{NO_2} C_6H_{11}OONO_2$$

Its formation was minimized by the exclusion of atmospheric oxygen but not suppressed completely; this was attributed to small amounts of oxygen liberated by the decomposition of the pentoxide.

The progress of reaction was followed by quantitative analyses for cyclohexane (3.41 and 3.50 μ bands), cyclohexyl nitrate (6.11 μ) and nitrocyclohexane (6.44 μ). Owing to solvent absorption, the analysis for nitrocyclohexane was made with wide slits and was least satisfactory. Cyclohexyl nitrate, however, could be estimated conveniently and rapidly in the range 0.1–0.001 *M*/l., and the velocity measurements below are mainly in the form of $d[C_6H_{11}ONO_2]/dt$. The spectra were recorded with a Perkin-Elmer spectrophotometer, model 21.

Results

The results of simultaneous analyses for nitrocyclohexane and cyclohexyl nitrate at different reaction times and under different initial conditions are shown in Fig. 1 where the experimental constancy of the ratio $[C_6H_{11}NO_2]/[C_6H_{11}ONO_2]$ over a wide range of nitrogen tetroxide concentration indicates that the rate-determining steps in the formation of the two compounds are *simultaneous side-reactions of the same order*. A plausible interpretation is that the union of a cyclohexyl radical with nitrogen dioxide can occur in two ways, namely



$$C_6H_{11} + NO_2 \begin{cases} \longrightarrow C_6H_{11}NO_2 \\ \longrightarrow C_6H_{11}ONO^* \xrightarrow{\text{fast}} C_6H_{11}ONO_2 \end{cases}$$

The velocity measurements do not specify the steps in the formation of cyclohexyl nitrate from C_6H_{11} and NO_2 but the simplest assumption is that the intermediate nitrite ester is oxidized directly to the nitrate.

$$NO_3 + C_6H_{11}ONO = NO_2 + C_6H_{11}ONO_2$$

In experiments made to test the plausibility of this reaction it was found that nitrogen pentoxide converts cyclohexyl nitrite quantitatively and very rapidly to nitrate. However, it may not be justified to overlook the fact that the union of a cyclohexyl radical with NO_2 liberates sufficient energy (~90 kcal.)[10] to bring about dissociation of the nitrite ester into cyclohexyloxy radicals and NO (requiring ~40 kcal.). In the event that this excess energy is not removed from the $C_6H_{11}ONO^*$ molecule by the solvent prior to dissociation a possible reaction scheme is

$$C_6H_{11}\cdot + NO_2 = C_6H_{11}ONO^* = C_6H_{11}O\cdot + NO$$
$$C_6H_{11}O\cdot + NO_2 = C_6H_{11}ONO_2$$

Measurements with nitrocyclohexane, cyclohexyl nitrate and chlorocyclohexane showed that none of these compounds was attacked by nitrogen pentoxide as rapidly as cyclohexane. From the kinetic viewpoint their oxidation could be neglected.[11]

Kinetics.—The factors governing the *initial* velocity of formation of cyclohexyl nitrate are analysed in Figs. 2 and 3. The order of reaction with respect to cyclohexane can be seen from Fig. 2 (curve A) where the initial velocity is plotted as a function of cyclohexane concentration at a constant initial concentration of nitrogen pentoxide; a small correction has been applied to the velocities to allow for minor variations of nitrogen tetroxide concentration. Similarly curve B (Fig. 2) shows the order of reaction with respect to nitrogen pentoxide. The retardation function for nitrogen tetroxide is illustrated in Fig. 3 where the square root of the analytical concentration of nitrogen tetroxide is plotted against the reciprocal initial velocity of formation of cyclohexyl nitrate. As the degree of dissociation of nitrogen tetroxide is small in the concentration and temperature range involved the analytical concentration is identified with $[N_2O_4]$.

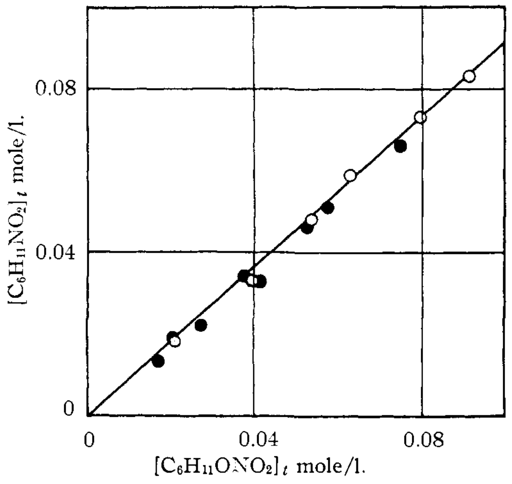


Fig. 1.—Formation of nitrocyclohexane and cyclohexyl nitrate in side reactions (temp. 20°, initial concn., *M*: C_6H_{12} = 0.2, N_2O_5 = 0.09–0.36, N_2O_4 = 0.004–0.025 (circles); 0.17–0.55 (dots)).

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(10) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1954, p. 272*f*.

(11) However, a proportion of the cyclohexane is degraded by the over-all reaction to products which include adipic acid[3] and 2-nitrocyclohexanone. The extent to which these more highly oxidized substances were formed could be seen from the ratio of moles formed of $N_2O_4:C_6H_{11}ONO_2$, which was usually in excess of the "theoretical" value of 1:1 required by the eq.

$$C_6H_{12} + 2N_2O_5 = C_6H_{11}ONO_2 + HNO_3 + N_2O_4$$

and in most expts was ~3:1. (Oxidation of the solvent accounted for only one-third of the excess). The results in the text indicate that 2-nitrocyclohexanone, for example, was formed by a side-reaction of a transient intermediate and not by direct oxidation of nitrocyclohexane or cyclohexyl nitrate.

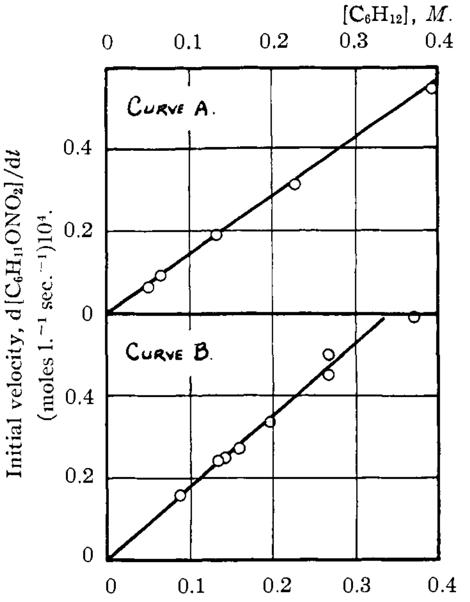

Fig. 2.—Orders of reaction with respect to cyclohexane and nitrogen pentoxide (temp. 20°, initial concn., *M:* (curve A, cyclohexane) $N_2O_5 = 0.194$, $N_2O_4 = 0.005–0.01$; (curve B, nitrogen pentoxide) $C_6H_{12} = 0.20$, $N_2O_4 = 0.006–0.017$).

Up to this point the results can be summarized by eq. 2

$$d[C_6H_{11}ONO_2]/dt = k[C_6H_{12}][N_2O_5]/(m + [N_2O_4]^{1/2}) \quad (2)$$

wherein k and m are constants at constant temperature. Values of the empirical constants (at 20°) and the parameters of the exponential factors (from additional data at 0°) are given in Table I, which is assembled from *experimental data* only.

TABLE I

Quantity	Source	Value at 20°	"Activation energy," kcal.
$[C_6H_{11}Cl]/[CCl_3NO_2]$	Eq. 1	2.5 ± 0.7	Low
$[C_6H_{11}NO_2]/[C_6H_{11}ONO_2]$	Fig. 1	0.90 ± 0.2	Low
k	Fig. 3 Eq. 2	$7.13 \pm 0.5 \times 10^{-5}$ $l.^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$	21.5 ± 0.5
m	Fig. 3 Eq. 2	0.016 ± 0.01 mole$^{1/2}$ l.$^{-1/2}$	—
m	Fig. 4	0.021 mole$^{1/2}$ l.$^{-1/2}$	-2 ± 1
K	Ref. 12	1.07×10^{-4} mole l.$^{-1}$	20.1 ± 1

Discussion

The mechanism proposed (*cf.* ref.[3]) is (eq. A–H)

$$N_2O_4 = NO_2 + NO_2 \text{ (equilibrium constant, } K)^{12}$$

$$N_2O_5 \overset{a}{=} NO_2 + NO_3 \quad (A)$$

$$NO_2 + NO_3 \overset{b}{=} N_2O_5 \quad (B)$$

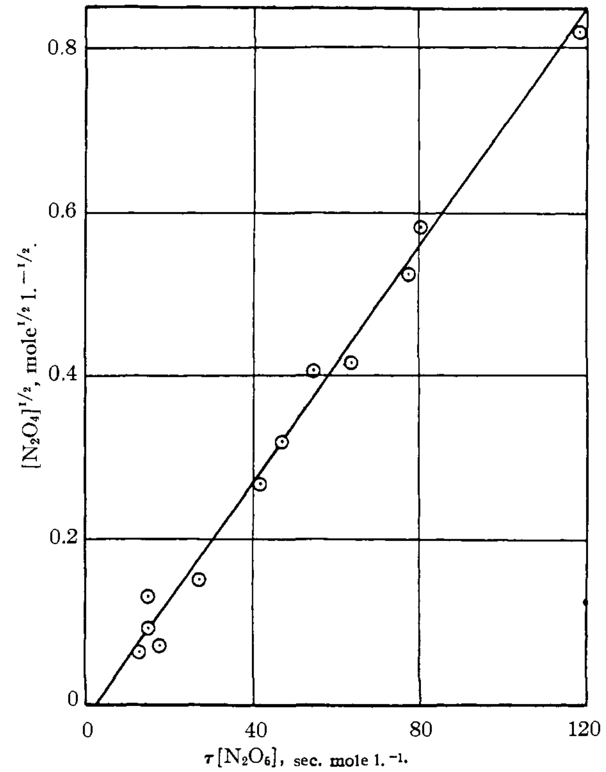

Fig. 3.—Retardation by nitrogen dioxide (temp. 20°, initial concn., *M:* $C_6H_{12} = 0.20$, $N_2O_5 = 0.087–0.308$; τ (abscissa) is the time in sec. for the conversion of 1% of the initial cyclohexane into cyclohexyl nitrate; the slope of the line is therefore $k \times 100$ and the intercept on the ordinate is $-m$).

$$C_6H_{12} + NO_3 \overset{c}{=} C_6H_{11} + HONO_2 \quad (C)$$

$$C_6H_{11} + NO_2 \overset{d}{=} C_6H_{11}NO_2 \quad (D)$$

$$C_6H_{11} + NO_2 \overset{e}{=} C_6H_{11}ONO^* \xrightarrow{\text{fast}} C_6H_{11}ONO_2 \quad (E)$$

$$C_6H_{11} + CCl_4 \overset{f}{=} C_6H_{11}Cl + CCl_3 \quad (F)$$

$$CCl_3 + NO_2 \overset{g}{=} CCl_3NO_2 \quad (G)$$

$$CCl_3 + NO_2 \overset{h}{=} CCl_3ONO^* \longrightarrow CCl_2O + NOCl \quad (H)$$

The occurrence of steps A and B in the gas phase is firmly established.[15] The steps C–H are exothermic with the possible exception of F which is nearly thermoneutral.[10] The heat of reaction of the rate-controlling step C (~ −10 kcal.) is sufficient to ensure that the reverse reaction (eq. C, reading right to left) is not kinetically significant. This result was verified experimentally, the addition of amounts of anhydrous nitric acid up to 0.3 *M* being found to have no influence on the rate of formation of cyclohexyl nitrate. Similarly, nitrogen dioxide had no oxidizing action on cyclohexane under the comditions of the present experiments.[16]

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[12] According to Holmes and Daniels,[13] $K = 3.01 \times 10^{-4}$ mole l.$^{-1}$ at 25°. Earlier measurements by Cundall[14] gave somewhat lower values which can be summarized by the eq.

$$\ln K = 25.20 - 20{,}100/RT$$

The value used in this paper, $K = 1.07 \times 10^{-4}$ mole l.$^{-1}$ at 20°, was calculated from Holmes and Daniels' measurement using $\Delta H = 20.1$ kcal. It may be noted here that the heat of dissociation in solution is significantly higher than the gas phase value, $\Delta H°_{298} = 14$ kcal.

[13] Quoted by E. D. Coon, THIS JOURNAL, **59**, 1910 (1937).

[14] J. T. Cundall, *J. Chem. Soc.*, **67**, 794 (1895).

[15] (a) H. S. Johnston, THIS JOURNAL, **73**, 4542 (1951); (b) R. A. Ogg, *J. Chem. Phys.*, **15**, 337, 613 (1947); **18**, 573 (1950).

[16] At higher temperatures (>200°) nitrogen dioxide initiates oxidation by a reaction analogous to C

$$RH + NO_2 = R + HONO$$

this step being followed by D and E.[17] The products of E suffer pyrolysis at the temperature necessary for initiation.

[17] A. D. Yoffe, *Research* (*London*), **6**, 12 S (1953).

As the reaction velocity over-all is never more than ten times faster than the rate of nitrogen pentoxide decomposition it can safely be assumed that the steady-state concentration of NO_3 is determined by eq. A and B. The stationary concentration of cyclohexyl radicals is, therefore

$$c(a/b)[C_6H_{12}][N_2O_5]/[NO_2]\{f + (d + e)[NO_2]\}$$

and hence

$$d[C_6H_{11}ONO_2]/dt = c(a/b)\{e/(d + e)K^{1/2}\}[C_6H_{12}][N_2O_5]/\{f/(d + e)K^{1/2} + [N_2O_4]^{1/2}\} \quad (3)$$

By comparison of the coefficients of eqn. 2 and 3

$$\begin{aligned} k\sqrt{K} &= c(a/b)\{e/(d + e)\} \text{ sec.}^{-1}\text{, and} \\ m\sqrt{K} &= f/(d + e) \text{ mole l.}^{-1} \end{aligned} \quad (4)$$

The experimental constants can now be used to evaluate a number of ratios of the coefficients *a*–*h*, and these are collected in Table II which is based on eq. A–H and on experimental quantities; no other assumptions are used.

TABLE II

Quantity	Source	Value at 20°	Pre-exponential factor	"Activation energy" kcal.
$c(a/b)$	$k\sqrt{K}$, d/e	1.40×10^{-6} sec.$^{-1}$		31.5
d/e	$[C_6H_{11}NO_2]/[C_6H_{11}ONO_2]$	0.90		Low
f/e	$m\sqrt{K}$, d/e	4×10^{-4} mole l.$^{-1}$	4×10^2	8
g/h	$[C_6H_{11}Cl]/[CCl_3NO_2]$	0.7		Low

Oxidation of the Solvent.—The oxidation of cyclohexane induces oxidation of the solvent to trichloronitromethane and phosgene. The extent of the attack is regulated by the constant *m* in eq. 2 which measures the proportion of cyclohexyl radicals reacting other than with nitrogen dioxide; nitrogen pentoxide alone has no oxidizing action on the solvent.

As one trichloromethyl radical is liberated per mole of chlorocyclohexane formed

$$(g + h)/g = [C_6H_{11}Cl]/[CCl_3NO_2] = 2.5 \text{ (eq. 1)} \quad (5)$$

Experimentally, the production of phosgene (and nitrosyl chloride) was followed by analysis for chloride ion after hydrolysis (see Exptl. section) and the ratio of *initial velocities* of formation of phosgene and cyclohexyl nitrate is, therefore

$$(1/3)[Cl^-]_t/[C_6H_{11}ONO_2]_t \quad (6)$$

where the subscript denotes concentration at time *t* within the initial rate period. If the steady-state assumption is made for CCl_3 radicals

$$[CCl_3]/[C_6H_{11}] = f/(g + h)K^{1/2}[N_2O_4]^{1/2} \quad (7)$$

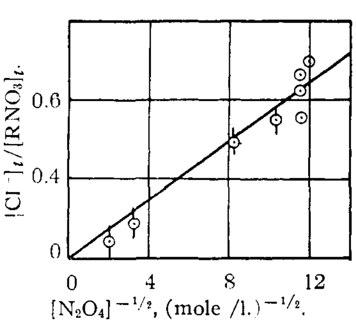

Fig. 4.—Relative initial rates of formation of phosgene and cyclohexyl nitrate (temp. 20°).

the ratio of the initial velocities of reactions H and F can, by combining eq. 6 and 7, be written

$$[Cl^-]_t/[C_6H_{11}ONO_2]_t = 3(f/e)\, h/(g + h)K^{1/2}[N_2O_4]^{1/2}$$

In Fig. 4, $[Cl^-]_t/[C_6H_{11}ONO_2]_t$ is plotted as a function of $[N_2O_4]^{-1/2}$; since $h/(g + h) = 0.6$ (eq. 5), the slope of a straight line drawn through the origin ($[N_2O_4] = \alpha$) is 1.8 $f/eK^{1/2}$. Introducing the graphical slope (7.2×10^{-2} moles$^{1/2}$ l.$^{-1/2}$ at 20°) and the value of *K*

$$f/e = 4.1 \times 10^{-4} \text{ moles l.}^{-1} \text{ at } 20°$$

At 0° phosgene formation was slightly enhanced, yielding an "activation energy" for $f/eK^{1/2}$ of -2 ± 1 kcal.

From f/e, *m* can be evaluated directly by the relations $m\sqrt{K} = f/(d + e)$ and $d/e = 0.9$. The value $m = 0.021$ agrees very satisfactorily with that obtained independently from the results in Fig. 3 ($m = 0.016$).

Absolute Velocity Coefficients.—Only ratios of the elementary velocity coefficients can be obtained directly from the experimental data. These are grouped in three sets which relate the coefficients *a*, *b* and *c*; *d*, *e* and *f*; *g* and *h*; there are no equations between coefficients in different sets. Only the first two sets are considered further, and in each case the absolute rate coefficients are evaluated with the assumption that a particular reaction proceeds with the same velocity in solution as in the gas phase. The results are in Table III.

In the first group, *c* could be evaluated if a/b, the dissociation constant of nitrogen pentoxide, were known. As the Arrhenius parameters for the decomposition of nitrogen pentoxide vapor and solution are very similar[5] it follows from the mechanism[15] that, if the reaction

$$NO_2 + NO_3 = NO + O_2 + NO_2$$

is *assumed* to have the same velocity in the two phases, the dissociation constant appropriate to the gas phase can be transferred to the solution. Hence $a/b = 3 \times 10^{-11}$ moles l.$^{-1}$ at 20°,[15a] and

$$c = 10^{13.2} \exp(-11{,}500/RT)$$

The pre-exponential factor of *c* is high for an elementary metathetical reaction, possibly owing to accumulation of errors in the exponential term formed from the same and differences of relatively larger quantities.

In the second group of coefficients it is *assumed* that the velocity of reaction *D* is of the same order of magnitude as the combination of methyl radicals with NO at high pressure in the gas phase.[18] Values of *e* and *f* follow directly from the ratios in Table II. It is in accord with experience from transfer coefficients in polymerization to allocate the "activation energy" of the ratio f/e entirely to reaction F. The frequency of bimolecular collisions between cyclohexyl radicals (assigned the same diameter as cyclohexane, *viz.*, $1.33 \times 10^{-8} V_m^{1/3} = 6.3$ Å., the effective diameter of the "cage" being 0.5 Å.) and carbon tetrachloride is 8×10^{11} l. mole^{-1} sec.$^{-1}$,[19] and the "maximum" pre-exponential fac-

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(18) A. F. Trotman-Dickenson, *Quart. Revs. Chem. Soc.*, **7**, 198 (1953).

(19) R. H. Fowler and N. B. Slater, *Trans. Faraday Soc.*, **34**, 81 (1938).

tor of the apparent first-order coefficient f is 8×10^{12} sec.$^{-1}$ The value deduced from the velocity coefficient and the activation energy (Table III) corresponds to a steric factor of 0.01 for reaction F.

TABLE III

Quantity	Source	Value at 20°, l. mole^{-1} sec.$^{-1}$	Pre-exponential factor	Activation energy kcal.
a/b	Gas phase[a]	3×10^{-11} mole l.$^{-1}$		20 ± 3
c	$c(a/b)$, a/b	5×10^{4}	2×10^{13}	11.5
d	Assumed	2×10^{8}		Low
e	d/e, d	2×10^{8}		Low
f	f/e, e	8×10^{4} sec.$^{-1}$	8×10^{10}[b]	8

[a] Ref. 15a. [b] 8×10^{9} l. mole^{-1} sec^{-1} if the "concn." of CCl_4 is factored out.

From the results in Table III it is easily seen that with the high concentration of nitrogen dioxide a number of intrinsically fast reactions are not important in this system. In a typical experiment ($[C_6H_{12}] = [N_2O_5] = [N_2O_4] = 0.2$ M) the concentrations of the various radicals relative to NO_2 are, at 20°

$[NO_3]/[NO_2]$	$[C_6H_{11}]/[NO_2]$	$[CCl_3]/[NO_2]$
3×10^{-7}	2×10^{-10}	6×10^{-12}

Thus the formation of cyclohexyl nitrate by direct radical union

$$C_6H_{11} + NO_3 = C_6H_{11}ONO_2$$

is insignificant compared with the reaction E through nitrite. Similarly, the solvent is the only species able to compete successfully with nitrogen dioxide for cyclohexyl radicals ($[CCl_4]/[NO_2] = 2 \times 10^3$ for $[N_2O_4] = 0.2$ M); the union of two cyclohexyl radicals, or of cyclohexyl and trichlormethyl radicals, is negligibly slow by comparison. Any latent tendency of the system toward a chain mechanism is suppressed by the nitrogen dioxide.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Proton Hyperfine Interactions in Paramagnetic Resonance of Semiquinones[1]

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Semiquinones formed by the oxidation of hydroquinones or the reduction of quinones in alkaline media have been studied by paramagnetic resonance absorption spectroscopy. The *p*-benzosemiquinone ion has been observed for the first time in solution; its existence has been established by examination of the structure of its paramagnetic resonance spectrum. It has been confirmed that certain structure observed in the paramagnetic resonance spectra of some free radicals is due to intramolecular magnetic hyperfine interaction between the unpaired electron and protons. The magnitude of the hyperfine interaction constant for the *p*-benzosemiquinone ion was found to be 6.54 ± 0.06 Mc./sec., and the magnitude of the constant for the durosemiquinone ion was found to be 5.28 ± 0.15 Mc./sec. Although theoretical interpretation of the magnitude of the interaction constants has not been satisfactory, it is believed that relative values of these constants can be interpreted in terms of relative odd-electron densities at the protons. The magnitude of the hyperfine interaction in the durosemiquinone ion may represent direct confirmation of the phenomenon of hyperconjugation. Paramagnetic spectra were observed from the *p*-tolusemiquinone ion, the 9,10-phenanthrenesemiquinone ion, and the radical formed from a mixture of benzil and benzoin. Evidence was found for the existence of two or more radicals in an alkaline alcoholic solution of *p*-benzoquinone exposed to the air.

Introduction

During the 1930's, it was demonstrated, principally by Michaelis and his co-workers,[2] that the bivalent oxidation of hydroquinones, or the reduction of quinones, proceeds through an intermediate compound containing an odd number of electrons, a semiquinone free radical. This conclusion was reached through the study of potentiometric oxidation–reduction titrations of these materials[3] and, in a few cases, by the measurement of the change in the magnetic susceptibility that took place during the course of a reduction of a quinone.[4] The magnetic method is too insensitive and slow for general applications, and the potentiometric method, which is capable of higher sensitivity than the magnetic technique, can only be applied to systems that produce a reasonably stable potential in an electromotive cell. Although this work showed that the stability of a semiquinone increases with increasing *p*H when no side reactions take place, many quinone systems are unstable in alkaline solution, and the simplest semiquinone, that of *p*-benzoquinone, was not detected in solution.

Considerable knowledge of the mechanism of the autoöxidation of hydroquinones has been obtained by Weissberger and his collaborators,[5] and it was postulated that a semiquinone intermediate is formed in these oxidations. Complete interpretation of the autoöxidations and of the general behavior of photographic developing agents is made dif-

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(1) Supported in part by Squier Signal Laboratory, U. S. Army Signal Corps. Presented before the Division of Physical and Inorganic Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

(2) For a review, including an extensive bibliography, see L. Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, 39 (1940). For later work, see references 2 and 3 below, and L. Michaelis, M. P. Schubert and S. Granick, THIS JOURNAL, **62**, 204 (1940); S. Granick, L. Michaelis and M. P. Schubert, *ibid.*, **62**, 1802 (1940); S. Granick and L. Michaelis, *ibid.*, **62**, 2241 (1940); L. Michaelis, S. Granick and M. P. Schubert, *ibid.*, **63**, 351 (1941); L. Micbaelis and S. Granick, *ibid.*, **63**, 1636 (1941); **66**, 1023 (1944); and S. Granick and L. Michaelis, *ibid.*, **69**, 2983 (1947).

(3) L. Michaelis and M. P. Schubert, *Chem. Revs.*, **22**, 437 (1938). See also, L. Michaelis in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, 2nd Ed., Vol. 1, Part II, p. 1713.

(4) L. Michaelis, G. F. Boeker and R. K. Reber, THIS JOURNAL, **60**, 202 (1938); L. Michaelis, R. K. Reber and J. A. Kuck, *ibid.*, **60**, 214 (1938); L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck and S. Granick, *ibid.*, **60**, 1678 (1938); L. Michaelis, *ibid.*, **63**, 2446 (1941); L. Michaelis and S. Granick, *ibid.*, **65**, 1747 (1943); **70**, 624, 4275 (1948).

(5) For a survey and references to earlier work, see J. E. LuValle and A. Weissberger, *ibid.*, **69**, 1567, 1576, 1821 (1947).