JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (Copyright, 1950, by the American Chemical Society)

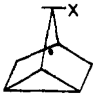
VOLUME 72 AUGUST 15, 1950 NUMBER 8

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

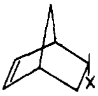
Solvolytic Reactivities of Nortricyclyl, Dehydronorbornyl and Norbornyl Halides. Possible Steric Requirements for Hyperconjugative Resonance[1]

BY JOHN D. ROBERTS, WINIFRED BENNETT AND ROSE ARMSTRONG

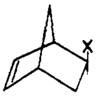
The present investigation is concerned with the determination and interpretation of the solvolytic reactivities of nortricyclyl (I), *endo*-dehydronorbornyl (II), *exo*-dehydronorbornyl (III), *endo*-norbornyl (IV) and *exo*-norbornyl (V) halides.



Ia, X=Cl
Ib, X=Br

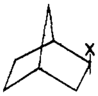


IIa, X=Cl
IIb, X=Br



IIIa, X=Cl
IIIb, X=Br

IVa, X=Cl
IVb, X=Br



Va, X=Cl
Vb, X=Br

This series of structurally similar compounds provides an almost unique opportunity to observe the relationship between stereochemistry and solvolytic reactivities in alicyclic halides.

With X as a given halogen there are considerable differences in reactivity between some of the members of the series. In aqueous ethanol (20% water–80% ethanol, by volume) the sequence of reactivities shown below can be inferred from the rate constants in Table I. This sequence is only qualitative since different temperatures were used for the bromides and chlorides and a single halogen as X was not used throughout.

$$\text{V} > \text{III} > \text{IV} \sim \text{II} \sim \text{I} \qquad (1)$$

A significant feature of the rate sequence is the greater reactivities of the *exo*-compounds, III and V, as compared to the corresponding *endo*-compounds, II and IV. Ths spread between *exo*- and *endo*-series is substantial although far less than the 10^5 fold difference between isobornyl and bornyl chlorides in 80% ethanol–20% water solution.[2,3] The products of the solvolysis of the *exo–endo*-isomer pairs in water (which was used in the product determinations to avoid complications due to formation of ethyl ethers) were the same; thus, II[4] and III both gave principally (>90%) 3-hydroxynortricyclene (VI)

TABLE I

SOLVOLYSIS RATES OF HALIDES (RX) IN 80% ETHANOL–20% WATER (BY VOLUME) SOLUTION

R	X	Temp., °C.	k_1, hr.$^{-1}$	% purity[a]
Nortricyclyl (I)	Br	55	0.015	100
endo-Dehydronorbornyl (II)	Br	55	.017	92[b]
	Cl	85	.017	97[c]
exo-Dehydronorbornyl (III)	Cl	85	.078	83[d]
endo-Norbornyl (IV)	Br	55	.020	80[b]
	Cl	85	.015	87[c]
exo-Norbornyl (V)	Br	55	.20	100
	Cl	85	.14	100

[a] Purity as indicated by analysis of reaction kinetics by the method of Brown and Fletcher, THIS JOURNAL, **71**, 1845 (1949). [b] Impurity was a more reactive bromide, presumably the *exo*-bromide. [c] Impurity was a more reactive chloride, presumably the *exo*-chloride. [d] Impurity was a less reactive chloride which from infrared spectrum and hydrogenation data seemed to be nortricyclyl chloride (Ia).

---

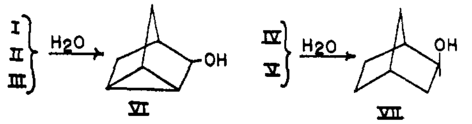
[1] (a) Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission. (b) Preliminary results on *exo*-norbornyl chloride were reported by Roberts, Urbanek and Armstrong, THIS JOURNAL, **71**, 3049 (1949).

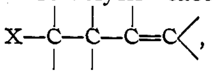
[2] Unpublished experiments by Mrs. Hildegarde Harris.

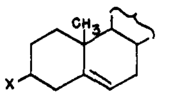
[3] Detailed discussion of the solvolysis rates of *exo*- *vs.* *endo*-isomers will be deferred until completion of another investigation.

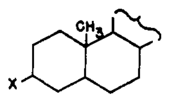
[4] Roberts, Trumbull, Bennett and Armstrong, *ibid.*, **72**, 3116 (1950).

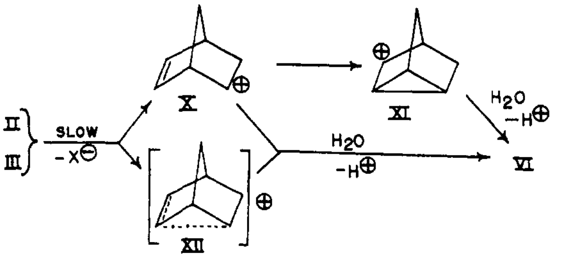
while IV and V gave *exo*-norborneol (VII).[5] VI is also obtained in the hydrolysis of I.[4]

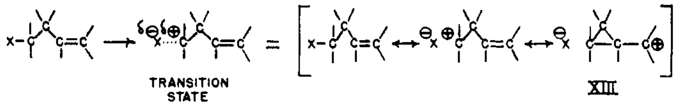


An interesting feature of sequence (1) is the slowness of the reactions of the unsaturated compounds, II and III, relative to those of the corresponding saturated compounds, IV and V. A quite different situation prevails in the solvolysis of cholesteryl (VIII) and cholestanyl (IX) compounds where the cholesteryl derivative reacts far more rapidly.[6] It is apparent from our results that the double bonds in II and III exert no very substantial "driving force" (of the type postulated for cholesteryl compounds)[6] during the ionization of the C–X bonds in the solvolysis reactions. It is significant that the reactions result with carbon skeleton rearrangement and the formation of VI showing that the double bond becomes involved in the over-all reaction if not in the rate-determining step. The reactions of II and III might be formulated as involving the isomerization of a dehydronorbornyl cation (X) to a nortricyclyl cation (XI) or the formation of the conjugate acid of VI by attack of water on cation X after the rate-determining step. An alternative scheme would have an intermediate ion such as XII[6] formed more or less directly in the rate-determining step. Since III is more favorably disposed structurally for the direct formation of a cation like XII than is II the larger solvolysis rate of III with respect to II could be accounted for on this basis. However, the effect on the rate is not large and the fact that the saturated compounds IV and V are actually somewhat faster than II and III shows that the driving force is small.[7] Irrespective of the actual product of the rate-determining step in solvolysis reactions of compounds of the type  $\mathrm{X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{C}{=}C\langle}$, the transition state for the ionization of the C–X bond can be considered to be stabilized to some extent by contributions of resonance forms such as XIII involving the neighboring double bond. It is reasonable to expect that the importance of forms like XIII should be influenced by the spatial relationship between the double bond and the reacting center. In this connection it is interesting to note that the double bond and reactive center are spatially quite different for cholesteryl derivatives VIII and the dehydronorbornyl halides, II and III. Models of the compounds reveal that C-3 in VIII is located more nearly "endwise" to the 5,6-double bond than the carbons holding the halogens in II and III are to the double bonds in these substances. While an *a priori* judgment as to the most favorable position is not easily made, the considerable reactivity of the cholesteryl derivatives indicates that the more endwise location results in an increased stabilization of the solvolysis transition state.

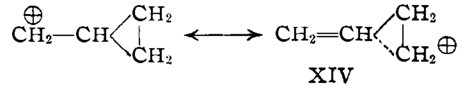

VIII


IX





Perhaps the most striking characteristic of sequence (1) is the extraordinarily low relative reactivity of nortricyclyl bromide (Ia). It has been found that other cyclopropylcarbinyl-type compounds are exceptionally reactive. Thus, cyclopropylcarbinyl chloride solvolyzes in aqueous ethanol 10^3–10^4 times faster than allylcarbinyl chloride[8] and the *i*-sterols are generally far more reactive than the corresponding cholesteryl or cholestanyl derivatives.[6,9] The high reactivity of cyclopropylcarbinyl chloride has been ascribed to stabilization of the cyclopropylcarbinyl cation by contributions of resonance forms such as XIV.[8] This resonance involving the C–C bond


$$\overset{\oplus}{CH_2}{-}CH\langle{}^{CH_2}_{CH_2} \longleftrightarrow CH_2{=}CH\langle{}^{CH_2}_{CH_2^{\oplus}}$$

XIV

of the cyclopropane ring is similar to the hyperconjugative resonance such as XV which has been proposed to account for the stability of alkyl-substituted carbonium ions. Actually, forms like

---

[5] Alder and Stein, *Ann.*, **514**, 211 (1934), and Komppa and Beckmann, *ibid.*, **512**, 172 (1934), have reported the formation of VII from the *endo*- and *exo*-norbornylamines with nitrous acid while Winstein and Trifan, THIS JOURNAL, **71**, 2953 (1949), obtained VII as the acetate from the acetolysis of *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates. Schmerling, *ibid.*, **68**, 195 (1946), found that Va gave *exo*-norborneol with water.

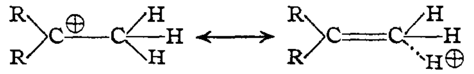
[6] See Winstein and Adams, *ibid.*, **70**, 838 (1948), for references and discussion.

[7] The situation is not unlike that found to exist in the solvolysis of the *p*-toluenesulfonate of 3-phenyl-2-butanol studied by Cram, THIS JOURNAL, **71**, 3863 (1949), where rearrangement occurs but no driving force is evident.

[8] Roberts and Mazur, paper in preparation.

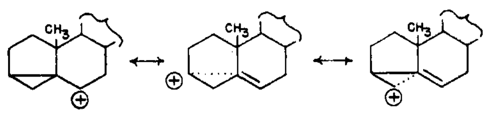
[9] *Cf.* Fieser and Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 256–261.

XIV should be expected to be more effective in stabilizing the cyclopropylcarbinyl cation than XV is for the usual alkylcarbonium ions because of the relative "looseness" of the electrons in the three-membered ring bonds. Resonance forms similar to XIV can be written for the stabilization of the *i*-cholesteryl cation XVI and the nortricyclyl cation X which from their appearance might be judged to be of comparable importance for each cation. Nonetheless, cation X is formed much less readily than XVI or the cyclopropylcarbinyl cation which fact suggests that the spatial relationship of the three-membered ring to the cationic center may be of considerable importance in determining the degree of resonance stabilization by forms XIV, XVIa, b and Xa.

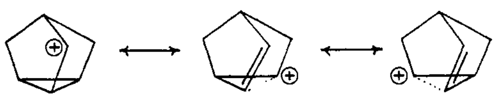


$R_2C^{\oplus}-CH_3 \longleftrightarrow R_2C{=}CH_2H^{\oplus}$

XV

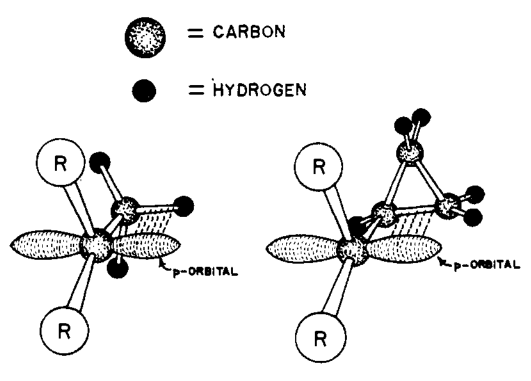


XVI XVIa XVIb



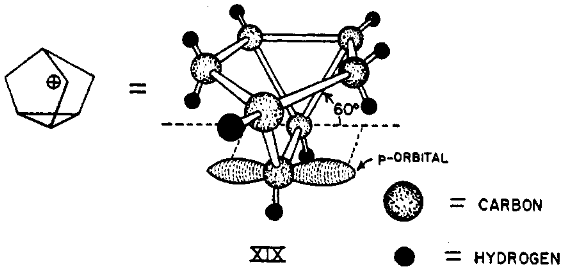
X Xa

So far, no clear statement of the steric requirements for hyperconjugative stabilization of carbonium ions has appeared although it has been stated without proof[10] that, for effective resonance interaction between an alkyl group and a benzene ring, the carbon atom which is directly attached to the benzyl group should be located *in the plane* of the ring. If it is considered that hyperconjugation in a carbonium ion can be ascribed to overlap of the vacant *p*-orbital of a planar cationic carbon with the σ-bonding orbitals of the adjacent carbon atom[11] then it seems likely that only one σ-bonding orbital on each group attached to the cationic carbon may be involved in the stabilization of a given ion. Thus, the overlap designated by XV and XIV may be represented by XVII and XVIII, respectively.



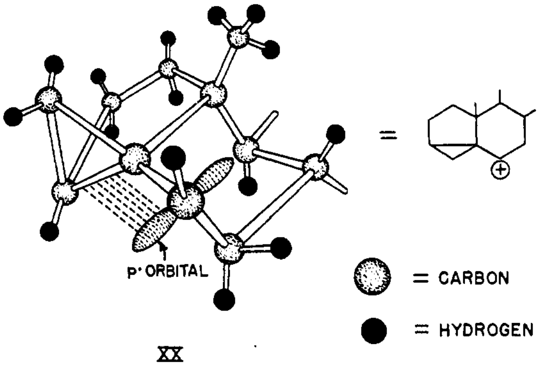
XVII XVIII

Similar formulation of the nortricyclyl cation X as in XIX indicates clearly that overlap of the vacant *p*-orbital with the bonding orbitals of the cyclopropane ring should not be very effective since the ring bonds are at about 60° angles to the *p*-orbital. A lack of resonance stabilization of this sort might be characterized as *steric inhibition of hyperconjugation.*



XIX

Application of these considerations to the *i*-cholesteryl cation XVI is particularly interesting. If *i*-cholesteryl derivatives are assigned the "chair" configuration for the B-ring, the *i*-cholesteryl cation may be represented by XX.



XX

The relationship of the vacant *p*-orbital at C-6 to the three-membered ring is such that the 3,5-bond is particularly well positioned for effective overlap corresponding to resonance form XVIa. Clearly, the orbital picture agrees with the experimental facts in that it indicates that the *i*-cholesteryl cation can be stabilized by hyperconjugative resonance. Significantly, the 4,5-bond is poorly situated for effective overlap and as a result resonance corresponding to hyperconjugation of this bond as in XVIb is not likely to be important. Consequently, it is not surprising that no products corresponding to XVIb have been reported from the reactions of cholesteryl or *i*-cholesteryl derivatives.

---

(10) Baddeley, Chadwick and Rawlinson, *Nature*, **164**, 834 (1949).

(11) *Cf.* Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 19.

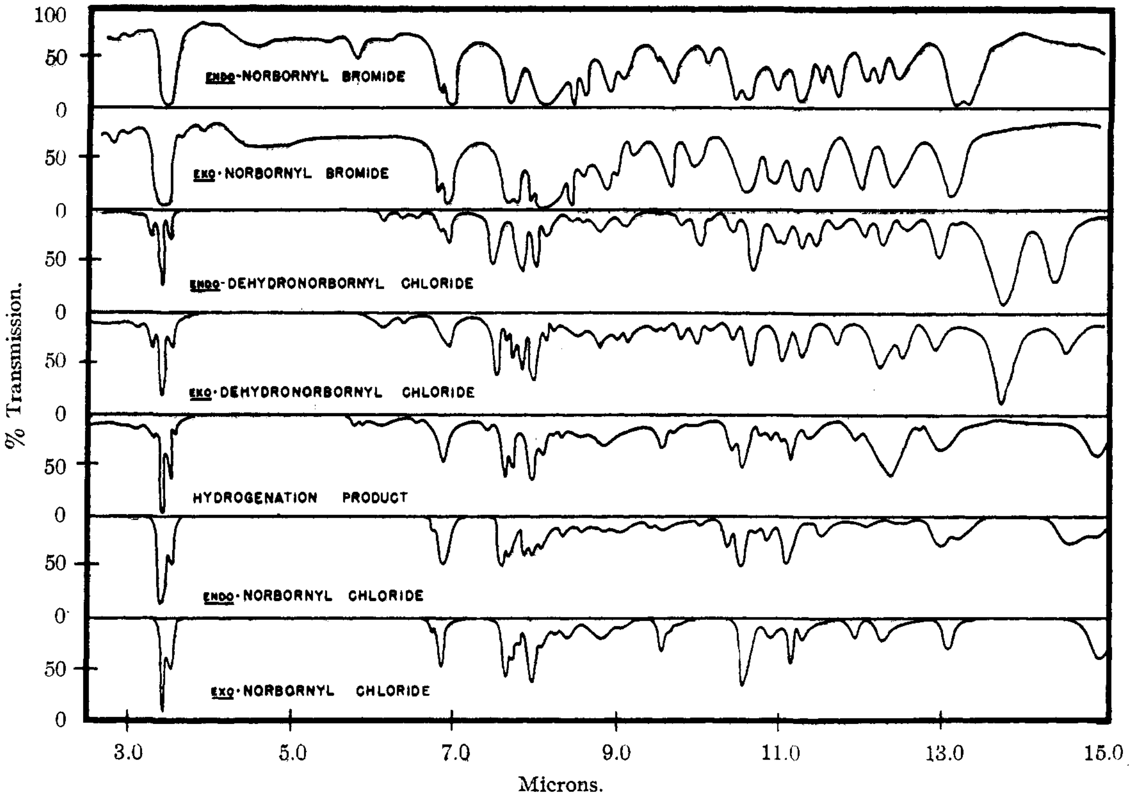


Fig. 1.—Infrared spectra: bromides determined with Perkin-Elmer spectrograph with NaCl prism, 0.1 mm. samples (no solvent); all others taken with Baird spectrometer with NaCl prism, 10% solutions in carbon disulfide except in the regions 4.2–5.0 μ and 6.2–7.2 μ where carbon tetrachloride was used as solvent.

Experimental

The preparations of several of the halides (Ib,[4] IIa,[4] IIb,[4] Va,[1] Vb[4]) used in the solvolysis rate studies have been described previously. The method of determining the solvolysis rates was the same as that used earlier.[1]

endo-**Norbornyl Halides** (IV) were obtained by hydrogenation in ethyl acetate over platinum oxide of the corresponding *endo*-dehydronorbornyl halides[4] prepared by the Diels–Alder reaction of vinyl halides and cyclopentadiene in sealed glass tubes. The impurities indicated by the kinetic analyses (Table I) are due to the slight non-stereospecificity of the Diels–Alder reaction.[4]

endo-Norbornyl bromide (IVb) had b. p. 69–70° (15.5 mm.) and n^{25}D 1.5198. The infrared spectrum is compared in Fig. 1 with that of the *exo*-isomer prepared by the addition of hydrogen bromide to norbornylene.[4] Hydrolysis of 4.0 g. of IVb by boiling for two and one-half days with 5.0 g. of lithium carbonate and 50 ml. of water gave 1.9 g. (76%) of *exo*-norborneol, m. p. 125.8–127.2°.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 48.43; H, 6.40.

endo-Norbornyl chloride had b. p. 51–53° (17 mm.), n^{25}D 1.4835, m. p. 28°. The infrared spectrum of the material is compared with that of *exo*-norbornyl chloride in Fig. 1.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.36; H, 8.49; Cl, 27.15. Found: C, 64.14; H, 8.48; Cl, 26.85.

exo-**Dehydronorbornyl Chloride (IIIa).**—It was reported previously[4] that the reaction of thionyl chloride with *endo*-dehydronorborneol gives principally nortricyclyl chloride (Ia). We now find that a somewhat modified procedure yields principally *exo*-dehydronorbornyl chloride (IIIa).

Redistilled thionyl chloride (14.7 g., 0.12 mole) was added dropwise to a stirred solution of 13.7 g. (0.12 mole) of *endo*-dehydronorborneol in 25 ml. of dry ether containing a few drops of pyridine. After the addition was complete, the mixture was refluxed for an hour and then distilled from a modified Claisen flask, b. p. 33–39° (8 mm.) On redistillation through a small Vigreux column 6.4 g. (42%) of chloride, b. p. 38° (9 mm.), n^{25}D 1.4909–1.4912, was obtained. The infrared spectrum of the product is shown in Fig. 1. The spectrum is distinctly different from that of the *endo*-isomer (IIa) and shows a weak band at 12.3 μ characteristic of the nortricyclene ring system.[4] On quantitative hydrogenation in ethyl acetate over platinum oxide, 81% of the theoretical quantity of hydrogen was absorbed and this result indicates that 19% of the material was nortricyclyl chloride. The hydrogenation product had b. p. 33° (8 mm.). Its infrared spectrum (Fig. 1) contained all of the bands of *exo*-norbornyl chloride as well as a band at 12.3 μ corresponding to the unreduced nortricyclyl chloride.

Hydrolysis of 1.7 g. of IIIa by boiling for three days with 1.1 g. of lithium carbonate and 15 ml. of water gave 1.0 g. (71%) of crude solid alcohol, m. p. 104–107°. The m. p. of 3-hydroxynortricyclene[4] is 108.8°. The product reacted with potassium permanganate in acetone and on quantitative hydrogenation absorbed 9% of the theoretical quantity of hydrogen calculated for a pure dehydronorborneol. The infrared spectrum of the material was practically identical with that of 3-hydroxynortricyclene[4] except for some weak absorptions which corresponded fairly well to the strong bands of *endo*-dehydronorborneol.

Summary

The solvolysis rates of some nortricyclyl,

endo- and *exo*-dehydronorbornyl and *endo*- and *exo*-norbornyl halides have been determined in aqueous ethanol solution.

The *exo*-isomers solvolyze considerably more readily than the *endo*-isomers. The double bond in the dehydronorbornyl halides appears to contribute less "driving force" in the ionization of the C–X bonds than does the 5,6-double bond in the solvolysis of cholesteryl derivatives.

Nortricyclyl bromide appears to be singularly unreactive relative to other substances containing the cyclopropylcarbinyl grouping. The cyclopropane ring in the nortricyclyl cation does not appear to contribute significantly to the stabilization of the ion. It is suggested that "steric inhibition of hyperconjugative-type resonance" may be involved.

CAMBRIDGE 39, MASS. RECEIVED JUNE 1, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE BARRETT DIVISION, ALLIED CHEMICAL & DYE CORPORATION]

The Decomposition of Cyclohexyl Hydroperoxide and the Peroxide-catalyzed Polymerization of Styrene*

BY ADALBERT FARKAS AND ELIO PASSAGLIA

Heretofore, most peroxide-catalyzed polymerization experiments have been carried out with benzoyl peroxide or derivatives of benzoyl peroxide.[1] In view of the rather complicated processes involved in the decomposition of benzoyl peroxide,[2] in the present work the polymerization of styrene was studied in the presence of cyclohexyl hydroperoxide since earlier experiments indicated that organic hydroperoxides are active polymerization catalysts.[3]

Preparation and Identification of Cyclohexylhydroperoxide.—The presence of a peroxide among the oxidation products of cyclohexane was reported by Mittag.[4] Cyclohexyl hydroperoxide was isolated and purified according to the method used by Farkas and Stribley[5] for the preparation of methylcyclohexyl hydroperoxide. The pure peroxide is a colorless liquid with a slight garlic-like odor. It is converted to 62.3 mole per cent. of cyclohexanol and 37.4 mole per cent. of cyclohexanone when reduced with aqueous solution of ferrous sulfate. The reduction with hydrogen in the presence of platinum oxide produces substantially pure cyclohexanol with a yield of 90 mole per cent.

Thermal Decomposition of Cyclohexyl Hydroperoxide.—The thermal decomposition of cyclohexyl hydroperoxide was investigated in various solvents at various concentrations and temperatures. Figure 1 shows the decomposition of cyclohexyl hydroperoxide in cyclohexane solution at 150° at two concentrations, the logarithm of the peroxide concentration being plotted against the time. At a low peroxide concentration, the decomposition proceeds according to a first order law. This law is, however, not obeyed at the higher concentration. The initial rate appears to be the same at both concentrations and it is possible that the acceleration observed at the higher concentration is due to the effect of the decomposition products of the peroxide on the rate of its decomposition.

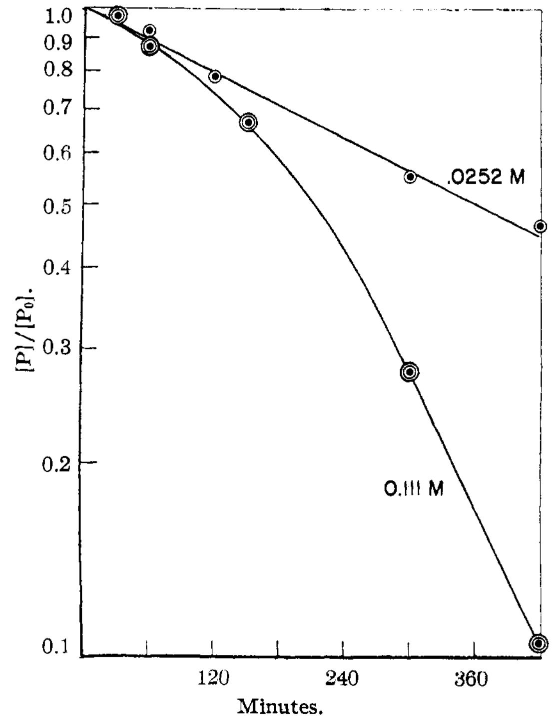


Fig. 1.—Decomposition of cyclohexyl hydroperoxide in 0.0252 and 0.111 *M* solutions in cyclohexane at 150°.

The first order velocity constants for the decomposition in cyclohexane are given in Table I

---

* This paper was presented before the Organic Division of the American Chemical Society in Atlantic City, New Jersey, September, 1949.

(1) See, *e. g.*, (a) S. G. Cohen, THIS JOURNAL, **67**, 17 (1945); (b) Price and Kell, *ibid.*, **63**, 2798 (1941); Redington, *J. Polymer Sci.*, **3**, 503 (1948).

(2) (a) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946); (b) Barnett and Vaughn, *J. Phys. Colloid Chem.*, **51**, 927 (1947); **51**, 942 (1947); (c) D. J. Brown, THIS JOURNAL, **62**, 2657 (1940).

(3) A. Farkas, A. F. Stribley and A. I. Smith, Petroleum Division, Am. Chem. Soc. Meeting at Atlantic City, New Jersey, April, 1946.

(4) Mittag, Scientific Zetko Exchange, "Catalytic Oxidation with Air in Liquid Phase. IV. Oxidation of Cyclohexane," P. B.-566, Department of Commerce, Office of Technical Services.

(5) A. Farkas and A. F. Stribley, U. S. Patents 2,430,864 and 2,430,865.