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Chlorination Studies of Unsaturated Materials in Nonpolar Media. II. Competition between Ionic and Free-Radical Reactions during Chlorination of Cyclohexene¹

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Chlorination of neat cyclohexene at 25° in the dark under nitrogen produced *trans*-1,2-dichlorocyclohexane (I), 3-chlorocyclohexene (II), and 4-chlorocyclohexene (III) in a ratio of 1.95:1.00:0.60; if cyclohexane was present, chlorocyclohexane (IV) became a significant product. External illumination led to no changes in product composition. This chlorination is interpreted as a solely free-radical reaction initiated by interaction between the reactants. Chlorination under oxygen eliminated III while I and II were now produced in a ratio of 3-4:1; under these conditions reaction apparently proceeds by means of the usual electrophilic attack of halogens on unsaturated molecules which can be observed in this case only in the presence of radical chain inhibitors. For a series of dark chlorinations under nitrogen, gradual dilution of cyclohexene with nonpolar solvents (1,1,2-trichlorotrifluoroethane, carbon tetrachloride, or cyclohexane) led to increasing importance of the ionic compared to the radical pathway. The dependence of the percentage of radical reaction on olefin concentration was determined and is attributed to an over-all higher kinetic order in olefin for the radical pathway due to participation of two or more molecules of olefin in the initiation process. Initiation of radical chlorination by interaction between olefins and chlorine is an example of a class of reactions between "even" molecules which form radicals under mild conditions; such reactions are discussed. For benzene and carbon disulfide as diluents, solvent effects on the radical pathway were observed which favor addition over total abstraction and abstraction at the 3-position of cyclohexene over that at the 4-position. The relative reactivities of the 3- and 4-hydrogens of cyclohexene and the saturated hydrogen of cyclohexane toward abstraction by chlorine atom at 25° were determined to be 1.20:0.72:1.00.

Introduction

Halogenation of olefins in nonpolar solvents, such as carbon tetrachloride, is a widely used organic reaction; however, attempts to investigate the mechanism have met with serious problems of catalysis by surfaces,

water, and hydrogen halides (particularly in the case of bromine)² and have given, at best, inconclusive results. In this and the succeeding paper³ we will consider specifically the mechanistic pathways for chlorination of unconjugated (π - π or p - π) olefins, either as neat liquids or in mixture with nonpolar diluents.

A considerable body of data⁴ suggests that simple olefins and chlorine do not undergo a rapid vapor phase reaction at ambient temperatures⁵ but do react vigorously as soon as a liquid phase of products develops in the reactor. Such reaction was found to produce predominantly addition products (55-65% and 75% from 1-butene and 2-butene, respectively)^{4a} except for olefins bearing two alkyl groups on the same olefinic carbon atom in which case allylic substitution products became dominant (93% 3-chloro-2-methyl-1-propene from isobutylene)^{4b}. Much of the existing data is difficult to interpret in mechanistic terms for two reasons: (1) most chlorinations have been carried to such great conversion that secondary products seriously complicate determination of the primary processes, and (2) the experimental variables of oxygen concentration and light intensity, found to be critical in the present study, have not been controlled. Taft⁷ has considered a number of possible heterolytic and homolytic mechanisms and has proposed that the observed addition: substitution ratios can best be correlated with olefin structure on the basis of an ionic mechanism. Electrophilic attack would produce a chlorocarbonium ion

(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p. 520.

(3) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2172 (1965).

(4) (a) H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939); (b) J. Burgin, W. Engs, H. P. A. Groll, and G. Hearne, *ibid.*, **31**, 1413 (1939); (c) D. V. Tishchenko and M. A. Shchigel'skaya, *J. Gen. Chem. USSR*, **7**, 1246 (1937); *Chem. Abstr.*, **31**, 6189 (1937); (d) D. V. Tishchenko, *J. Gen. Chem. USSR*, **8**, 1232 (1938); *Chem. Abstr.*, **33**, 4190 (1939).

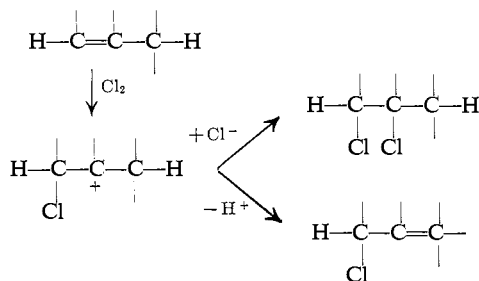
(5) There is an efficient homogeneous process at higher temperatures (300-600°) which appears to involve radical chain reactions initiated by thermal dissociation of chlorine. This process produces chiefly allylic chlorides because, although chlorine atom apparently both adds to the double bond and abstracts allylic hydrogen atoms, the addition process is reversible whereas the abstraction process is not; cf. H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939), and D. V. Tishchenko and A. N. Churbakov, *Zh. Prikl. Khim.*, **19**, 243 (1946), as well as ref. 6a.

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) p. 359; (b) pp. 352-369; (c) pp. 48-53, 241, 242.

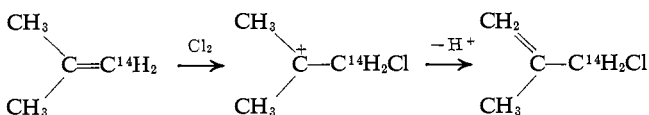
(7) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).

(1) Reported in preliminary form by M. L. Poutsma, *J. Am. Chem. Soc.*, **85**, 3511 (1963). For part I, see M. L. Poutsma and R. L. Hinman, *ibid.*, **86**, 3807 (1964).

which would either collapse with chloride ion to produce the addition product or undergo proton loss to produce the allylic substitution product. The tendency for branched olefins to favor substitution seemed consistent with their greater number of available α -hydrogens and with the known tendency of tertiary carbonium ions to give larger $E1:S_N1$ ratios in solvolysis studies than secondary carbonium ions.⁸ Such a pathway is generally accepted as the mechanism of chlorination of



olefins in *polar* solvents such as acetic acid or alcohols.⁹ Extensive kinetic data, particularly of Robertson and co-workers,¹⁰ support this concept of electrophilic chlorination in polar media. However, almost all the olefins studied in detail were those in which the reactivity of the double bond was reduced by the presence of electron-withdrawing groups so as to achieve conveniently measurable rates; few data are available for simple olefins in polar solvents. Support for operation of the Taft⁷ mechanism in *nonpolar* solvents, in the specific case of isobutylene, was provided by labeling experiments.¹¹ The methallyl chloride produced by chlorination of 1-C¹⁴ isobutylene contained essentially all the label at the chlorine-bearing carbon atom and none at the terminal olefinic carbon atom; this result rules out any symmetrical intermediate such as an allylic radical.



Such an ionic route for chlorination of olefins in nonpolar solvents appears to have been rather generally accepted for all olefins (although it has been criticized as being a serious oversimplification⁹). However, several early observations by Stewart¹² and others^{4a,13} are not only not accommodated by this ionic mechanism but also are suggestive of free-radical intermediates.

Stewart and Smith^{12a} attempted to study the vapor phase reaction of chlorine and ethylene at ambient

temperatures but found that the major portion of reaction occurred in liquid films of product deposited on the walls of the vessel and that two reactions appeared to occur simultaneously: addition to form dichloroethane and substitution on this product to form trichloroethane. The extent of this substitution reaction could be sharply reduced by oxygen but not by nitrogen or water vapor. More dramatic evidence for this "induced substitution reaction" was presented by Stewart who found that dark chlorination of ethylene in benzene^{12b} or pentane^{12c} solution produced considerable amounts of *sym*-hexachlorocyclohexane and chloropentanes, respectively, under conditions where benzene and pentane alone were stable towards chlorine. Further studies^{12d} with a variety of olefins suggested that the amount of "induced substitution" of paraffins which accompanied the chlorination of simple olefins was enhanced by increased olefin concentration and decreased chlorine concentration. Stewart concluded that substitution was the result of further reactions of "activated" addition products formed from chlorine and the olefin which led to intermediates similar to those present during photochlorination of saturated molecules, a process now known to proceed through free radicals.^{6b}

We have found that much of the apparent confusion concerning olefin chlorination is due to operation of two competing reaction pathways, one polar and one radical, which are involved in chlorination of olefins in *nonpolar* solvents; the balance between these pathways is determined not only by olefin structure but also by olefin concentration. The radical reactions are not artifacts due to adventitious initiators such as light or impurities but are a direct consequence of the chemical nature of the reactants. This paper will describe an intensive study of the chlorination of cyclohexene as a model compound while the succeeding paper³ will describe a more extensive study of the chlorination of alkylethylenes.

Previous studies of cyclohexene chlorination^{14,15} have shown that the major product is *trans*-1,2-dichlorocyclohexane accompanied by varying amounts of 3-chlorocyclohexene. Bloomfield¹⁶ conducted the chlorination in the absence of oxygen and strong light and found that the isolated substitution product released only 80% of its chlorine when treated with silver nitrate; therefore 4-chlorocyclohexene was assumed to have been formed although it was neither isolated nor identified. Kuriacose¹⁷ chlorinated cyclohexene in carbon tetrachloride solution at 0° and concluded that addition and substitution were parallel processes of the same kinetic order in olefin and that both free-radical and ionic processes might be occurring; however, no products were isolated from these reactions which were run to very high conversion.

Results

Product Dependence on Experimental Conditions. Passage of chlorine diluted with nitrogen into neat

(14) W. Markownikoff, *Ann.*, 302, 1 (1898); M. Mousserant, F. Granger, and R. Valetier, *Bull. soc. chim. France*, 244 (1946); H. Böhme and R. Schmitz, *Chem. Ber.*, 88, 357 (1955).

(15) (a) B. Carroll, D. G. Kubler, H. W. Davis, and A. M. Whaley, *J. Am. Chem. Soc.*, 73, 5382 (1951); (b) H. C. Stevens and O. Grummitt, *ibid.*, 74, 4876 (1952).

(16) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(17) J. C. Kuriacose, *Indian J. Appl. Chem.*, 22, 181 (1959).

(8) E. D. Hughes, C. K. Ingold, S. Masterman, and B. J. McNulty, *J. Chem. Soc.*, 899 (1940).

(9) For a review of halogenation, see P. B. D. de la Mare, *Quart. Rev. (London)*, 3, 126 (1949).

(10) E. P. White and P. W. Robertson, *J. Chem. Soc.*, 1509 (1939); I. D. Morton and P. W. Robertson, *ibid.*, 129 (1945); I. Hartman and P. W. Robertson, *ibid.*, 891 (1945); B. E. Swedlund and P. W. Robertson, *ibid.*, 630 (1947); H. P. Rothbaum, I. Ting, and P. W. Robertson, *ibid.*, 980 (1948).

(11) W. Reeve, D. H. Chambers, and C. S. Prickett, *J. Am. Chem. Soc.*, 74, 5369 (1952).

(12) (a) T. D. Stewart and D. M. Smith, *ibid.*, 51, 3082 (1929); 52, 2869 (1930); (b) T. D. Stewart and M. H. Hanson, *ibid.*, 53, 1121 (1931); (c) T. D. Stewart and B. Weidenbaum, *ibid.*, 57, 2036 (1935); (d) T. D. Stewart and B. Weidenbaum, *ibid.*, 58, 98 (1936); (e) T. D. Stewart, K. Dod, and G. Stenmark, *ibid.*, 59, 1765 (1937).

(13) R. M. Deanesly, U. S. Patent 1,952,122 (1934); *Chem. Abstr.*, 28, 3422 (1934).

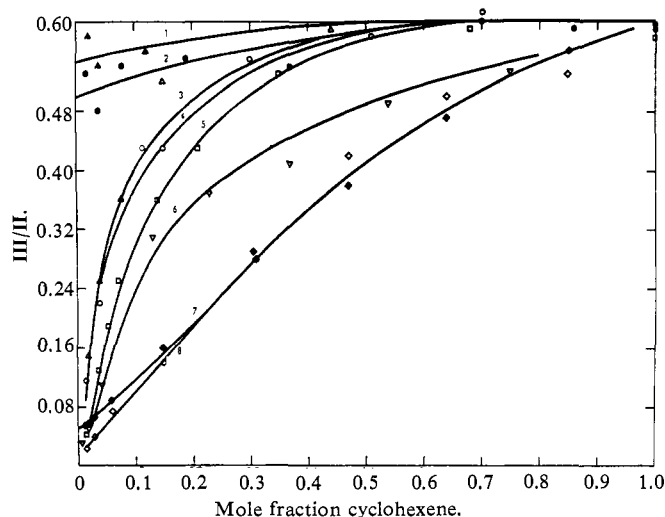
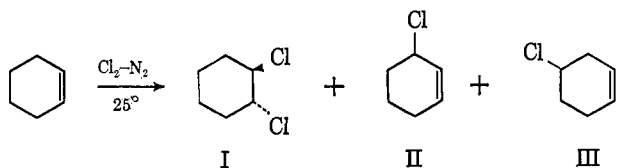


Figure 1. Effect of cyclohexene concentration on III/II from chlorination under nitrogen at 25° (open symbols, darkness; solid symbols, illuminated): Δ (1,3), carbon tetrachloride diluent; \circ (2,4), 1,1,2-trichlorotrifluoroethane; \square (5), cyclohexane; ∇ (6), carbon disulfide; and \diamond (7,8), benzene.

cyclohexene, previously well flushed with nitrogen, in the dark at 25.0° produced, at low conversion, three major products: *trans*-1,2-dichlorocyclohexane (I), 3-chlorocyclohexene (II), and 4-chlorocyclohexene (III) in the ratio of 1.95:1.00:0.60 as determined by g.l.c. analysis. The substitution products were identified by isolation and comparison with authentic samples: II obtained from photochlorination of cyclohexene with *t*-butyl hypochlorite¹⁸ and III obtained from dehydration of 4-chlorocyclohexanol.¹⁹ The reaction was very rapid, no chlorine color ever developing in solution. Illumination with sun lamps during reaction produced no changes in product ratios. However, replacement of the nitrogen carrier gas by oxygen eliminated production of III, whereas I and II were formed in a reaction still too rapid to allow any chlorine color to develop in solution. Similar dark chlorination under nitrogen of mixtures of cyclohexene and cyclohexane produced chlorocyclohexane (IV)²⁰ along with I, II, and III; use of oxygen eliminated production of IV as well as III. Products III and IV could also be essentially eliminated by conducting the chlorination in polar solvents; in acetonitrile and acetone, I and



II were produced along with unidentified products presumably due to solvent participation in the reaction.²¹ From these observations, it seems clear that III and IV are produced by a free-radical chain process (which would produce I and II concurrently) which can

(18) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

(19) S. F. Birch, R. A. Dean, and H. J. Hunter, *J. Org. Chem.*, **23**, 1026 (1958).

(20) No IV is produced by addition of hydrogen chloride to cyclohexene under these conditions.

(21) Amide formation during chlorination of propylene in acetonitrile has been reported by G. Sumrell, R. G. Howell, B. M. Wyman, and M. C. Harvey, *J. Org. Chem.*, **30**, 84 (1965).

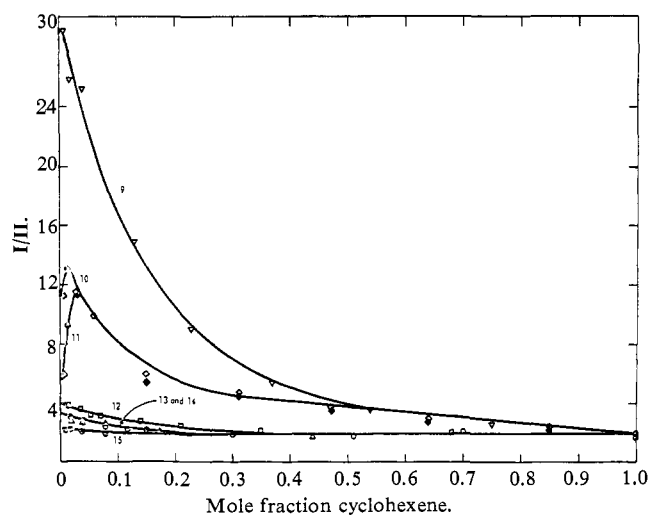
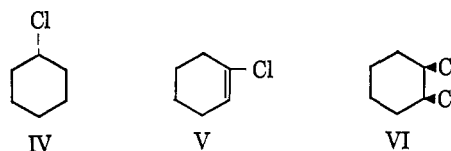


Figure 2. Effect of cyclohexene concentration on I/II from chlorination under nitrogen at 25° (open symbols, darkness; solid symbols, illuminated): Δ (13), carbon tetrachloride diluent; \circ (14,15), 1,1,2-trichlorotrifluoroethane; \square (12), cyclohexane; ∇ (9), carbon disulfide; and \diamond (10,11), benzene.

be inhibited by oxygen or superseded in polar solvents by a more polarity-dependent process which leads to only addition and allylic substitution products, presumably by the path suggested by Taft.⁷ Attack on the completely saturated substrate, cyclohexane, is compelling evidence for the presence of free-radical chains. However, determination of the relative contributions of the two reaction pathways to the uninhibited dark reaction required further data.

Two minor products were present in amounts large enough to detect and identify with reasonable certainty by g.l.c. retention times but too small to isolate or to measure accurately: 1-chlorocyclohexene (V) and *cis*-1,2-dichlorocyclohexane (VI). Small amounts of V (<5% of II) seemed to be present both in reactions described below as entirely radical and in those entirely ionic. The addition product was >99% *trans* under ionic conditions, but up to 4% *cis* addition was observed under radical conditions.



Concentration Effects in Trichlorotrifluoroethane. A discovery, which helped to clarify the chlorination behavior, was the remarkable dependence of product distributions on cyclohexene concentration when non-polar diluents were added. As mixtures of cyclohexene and 1,1,2-trichlorotrifluoroethane containing progressively less and less olefin were chlorinated under otherwise identical conditions in the dark under nitrogen at 25.0°, the ratio III/II decreased from 0.60 to values approaching zero while the ratio I/II increased from 1.95 to values approaching 3. This behavior is shown in curve 4 of Figure 1 and curve 14 of Figure 2. However, most of this marked decrease in production of III and modest increase in production of I with decreasing olefin concentration could be eliminated by illumination of the system with three 275-w. sun

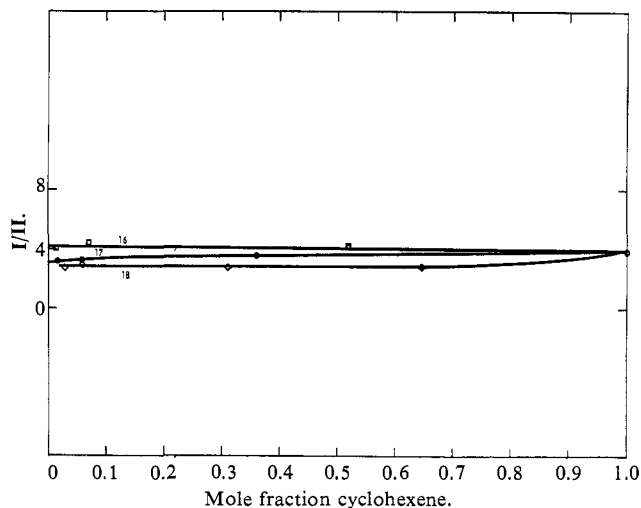


Figure 3. Effect of cyclohexene concentration on I/II from dark chlorination under oxygen at 25°: ○ (17), 1,1,2-trichlorotrifluoroethane diluent; □ (16), cyclohexane; and ◇ (18), benzene.

lamps placed at 6–9 in.; this is shown in curve 2 of Figure 1 and curve 15 of Figure 2. For oxygen-inhibited runs in which only I and II were produced, the I/II ratio decreased slightly from values near 4 in neat cyclohexene to values near 3 in very dilute cyclohexene; curve 17 of Figure 3, the ordinate of which is on the same scale as that of Figure 2 for proper comparison, shows this change. To account for this behavior, it is proposed that, as the concentration of olefin decreases in the uninhibited runs, the fraction of the total reaction proceeding through radical intermediates is decreasing; the amount of the solely radical product III produced is especially diagnostic of such behavior. In very dilute solutions of olefin, little III is formed (and attack on added cyclohexane is small, *vide infra*) while I and II are produced in a ratio similar to that which would have been obtained from a parallel run under oxygen; hence reaction is predominantly ionic. However, as the olefin concentration increases, the amount of III produced increases as would be expected if a gradually increasing proportion of the total reaction were proceeding through the radical pathway. The fact that the ratio III/II becomes asymptotic to the value 0.60 at values of mole fraction cyclohexene >0.50, coupled with the fact that the value 0.60 cannot be exceeded even under illuminated conditions, suggests that the ratio 0.60 is characteristic of an exclusively radical pathway and that all ionic reaction has been eliminated at this point. Hence it is concluded that *the dark reaction of chlorine with neat cyclohexene at 25.0°, even with no attempt at initiation, is entirely free radical in nature.*

The behavior of III/II with olefin concentration, as illustrated in Figure 1, would arise if the ionic and radical reactions proceeded with different kinetic orders with respect to olefin and/or chlorine. The experiments depicted in Figures 1 and 2 were conducted by introducing chlorine at a rather constant rate; hence, the average chlorine concentration may well have varied from run to run as the concentration of cyclohexene was varied. Therefore experiments were conducted to determine the effect of changing the chlorine input rate (and hence hopefully the average chlorine

concentration) at constant olefin concentration; results are summarized in Table I for runs with cyclohexane as diluent (*vide infra*). No significant effect was seen over a 10- to 20-fold change in input rate.

Table I. Effect of Chlorine Input Rate on III/II from Chlorination of Cyclohexene at 25.0° under Nitrogen in the Dark

Mole fraction of cyclohexene ^a	Input time, ^b min.	III/II
0.67	2.5	0.62
	8.0	0.56
	13	0.59
0.17	2.5	0.42
	9.0	0.42
	24	0.42
0.063	1.0	0.19
	8.0	0.19
	26	0.20

^a Cyclohexane diluent. ^b Chlorine (5 mmoles) into a 15-ml. reaction volume.

It appeared important at this point to study two less obvious variables: (1) the dependence of product ratios on chance impurities in cyclohexene, and (2) dependence of product ratios on the gross features of the reaction vessel. In Table II are summarized results

Table II. Effect of Impurities on III/II from Chlorination of Cyclohexene^a at 25.0° under Nitrogen in the Dark

Reaction conditions	III/II
Purified cyclohexene ^b	0.43
Commercial cyclohexene	0.42
Aerated cyclohexene	0.40
<i>t</i> -Butyl hydroperoxide added ^c	0.31
Reaction mixture saturated with water	0.42
Hydrogen chloride carrier gas	0.39

^a Mole fraction 0.19 in C₂F₆Cl₃. ^b Distilled from sodium and passed through alumina under nitrogen. ^c 5% of amount of cyclohexene.

typical of those obtained concerning factor 1 at a concentration of olefin such that variations in the ionic:radical ratio would be manifested in significant changes in III/II. All normal reactions were carried out with cyclohexene distilled from sodium; occasionally it was also passed through alumina directly into the reaction vessel under nitrogen. Such material gave results no different from untreated commercial material which gave strong tests for the presence of peroxides. Use of partially autoxidized cyclohexene or addition of small amounts of *t*-butyl hydroperoxide gave results which indicated that, if peroxides were having an effect at all, they were behaving as mild inhibitors rather than initiators of radical chains. This result is not unexpected for any peroxy or alkoxy radicals formed by chain transfer of alkyl radicals with hydroperoxides rather than with chlorine would be less reactive towards the substrate olefin than chlorine atom; this would lead to a greater concentration of radicals and enhanced bimolecular termination (chain shortening). Possible polar catalysts gave no measurable effect; neither saturation of the reaction mixture with water nor use of hydrogen chloride as a carrier gas changed the III/II ratio beyond experimental error.

With respect to factor 2, all normal reactions were conducted in an ordinary Pyrex flask equipped with a Teflon magnetic stirring bar and water-cooled condenser, and the gases (chlorine plus nitrogen, oxygen, or hydrogen chloride) were introduced through a small capillary inlet tube at a velocity sufficient to inject the gas stream well into the reaction volume. Results were invariant for a number of inlet capillaries of various over-all sizes and bores, both common and Pyrex glass, and for a number of flasks including an all-Teflon system. There was no effect of rate or even absence of stirring beyond that provided by the incoming gas. However, there was a pronounced decrease in the amount of III produced if the gases were introduced through a fritted glass inlet tube or through the shaft of a stirrer having a large unpolished glass surface.

Dark chlorination of neat cyclohexene under nitrogen was carried out at temperatures as low as -78° ; here the reaction was still too rapid to allow visual observation of chlorine in solution. The III/II and I/II ratios were 0.45 and 3.3 at -78° compared with 0.60 and 1.95 at 25.0° .

Chlorination in Other Nonpolar Solvents. The effects of four other solvents on the chlorination of cyclohexene were studied. The dependence of III/II on olefin concentration for dark chlorination under nitrogen in trichlorotrifluoroethane, carbon tetrachloride, cyclohexane, benzene, and carbon disulfide is shown in curves 4, 3, 5, 8, and 6, respectively, of Figure 1; the effect of illumination for chlorinations in trichlorotrifluoroethane, carbon tetrachloride, and benzene is shown in curves 2, 1, and 7. Corresponding effects on I/II are shown in Figure 2. Two general types of solvent behavior are noted. The noncomplexing solvents, carbon tetrachloride and cyclohexane, gave results very similar to those in trichlorotrifluoroethane with respect to both III/II and I/II. However, the complexing solvents,²² benzene and carbon disulfide, led to a more rapid decrease in III/II from the limiting 0.60 value which commenced at olefin concentrations well above mole fraction 0.5; this decrease in III/II in benzene solvent could not be counteracted by illumination until rather low concentrations of olefin were reached. Benzene and carbon disulfide caused I/II to increase sharply and then to pass through a maximum as the olefin concentration was decreased (curves 11 and 9). Finally in Figure 3, the small effects of the various solvents on I/II during oxygen-inhibited runs are shown.

Additional information can be obtained from the amount of chlorocyclohexane (IV) produced in the runs with cyclohexane as diluent. The relative reactivities of cyclohexene and cyclohexane, per hydrogen, with respect to the two exclusively radical products III and IV only (as determined experimentally from the expression $3(\text{III})(\text{cyclohexane})_0/(\text{IV})(\text{cyclohexene})_0$ where 0 signifies initial concentrations)²³ were unaf-

(22) These solvents are "complexing" in the sense that they are believed to form complexes with chlorine atom; this behavior results in their ability to change rather markedly the selectivity of free-radical chlorinations; see (a) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958); (b) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959); (c) M. L. Poutsma and R. L. Hinman, *ibid.*, **86**, 3807 (1964).

(23) This expression is a good approximation of the exact logarithmic expression since conversions were at all times $< 10\%$ of the amount of

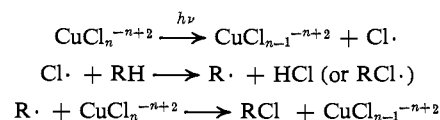
affected by large changes in the relative proportions of the two reactants for dark chlorinations under nitrogen as shown in Table III. These data further support the free-radical hypothesis.

Table III. Relative Reactivities of a 4-Cyclohexenyl and a Cyclohexyl Hydrogen Atom toward Chlorine Atom at 25.0°

Mole fraction of cyclohexene	(cyclohexane) ₀ (cyclohexene) ₀	Relative reactivity ^a
0.68	0.47	0.76
0.35	1.87	0.74
0.21	3.75	0.72
0.14	6.11	0.72
0.071	13.1	0.72
0.053	17.8	0.72
0.036	27.1	0.71
0.014	69.5	0.68
		Av. 0.72

^a Determined from $3(\text{III})(\text{cyclohexane})_0/(\text{IV})(\text{cyclohexene})_0$.

Other Halogenating Agents. The large amount of attack at the saturated position of cyclohexene (to produce III) compared to allylic attack (to produce II) observed for chlorine atom prompted a brief survey of other radical halogenating agents. Kochi²⁴ reported that a variety of hydrocarbons could be chlorinated by photolysis of cupric chloride-lithium chloride mixtures in acetonitrile solution. Since the selectivity observed with alkanes was similar to that for photochlorination, the following tentative mechanism was proposed. Cyclohexene was reported to give 37%



substitution as measured by titration of hydrogen chloride and the isolated substitution product was designated 3-chlorocyclohexene (II). Our re-examination shows that the substitution product is actually a mixture of II and III with III/II = 0.55–0.70. This value is only approximate since some fractionation may have occurred during work-up with water prior to g.l.c. analysis. Since chlorination of cyclohexene with molecular chlorine in the relatively polar acetonitrile gave no III, the above results support the Kochi mechanism which postulates generation of chlorine atoms rather than chlorine molecule from photolysis of cupric chloride.

Quantitative g.l.c. examination of the products from photochlorination of cyclohexene and 1:1 cyclohexene-cyclohexane mixtures with *t*-butyl hypochlorite gave the following relative reactivities per hydrogen for abstraction by *t*-butoxy radical at 25.0° : 3-cyclohexenyl:4-cyclohexenyl:cyclohexyl:13.8:0.67:1.00.²⁵

either starting material and hence the concentrations of cyclohexane and cyclohexene were essentially constant during a run.

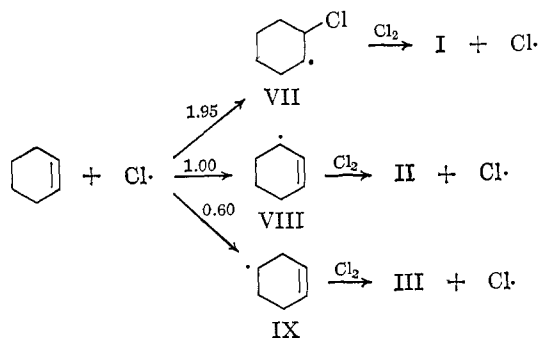
(24) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 2121 (1962).

(25) Walling and Thaler¹⁸ found the relative reactivities of cyclohexene and cyclohexane per molecule to be 8.5:1.0 at 40° based on disappearance of starting materials. If one assumes that addition of *t*-butoxy radicals to cyclohexene is negligible compared to abstraction, this value can be compared to our value of 4.8:1.0 per molecule. However, our determinations were performed at only a single olefin concentration and it is not known whether these relative rates may be concentration dependent.

Bromination of cyclohexene with N-bromosuccinimide initiated by illumination at 77° gave a monosubstitution product which was >99% a single isomer to g.l.c. on a polypropylene glycol column and was identified as 3-bromocyclohexene by isolation. To check that some 4-bromocyclohexene was not concealed by the major peak, bromination was repeated with *t*-butyl hypobromite²⁶; g.l.c. analysis of this reaction mixture under identical conditions revealed a new product slightly separated from the major product and consisting of ~5% of the quantity of the latter. Since this bromination involves *t*-butoxy radicals as the chain-carrying species and should therefore have given a 4:3- isomer ratio identical with that from *t*-butyl hypochlorite chlorination (4.5% of the 4- isomer), the result is consistent if the minor product is the suspected 4-bromocyclohexene.

Discussion

Product Composition. The very existence of 4-chlorocyclohexene (III) as a significant product from the rapid dark chlorination of cyclohexene under nitrogen (along with products I and II), combined with the observed elimination of III by either oxygen or polar solvents to leave only I and II as major products, shows that this chlorination involves free-radical reactions. The decrease in III compared to II caused by dilution with inert nonpolar solvents shows that a competition between radical and ionic processes exists and that the ionic reaction becomes increasingly important at low concentrations of olefin since II can be produced by either process whereas III is derived only from the radical pathway. As shown earlier, the effects of illumination (Figures 1 and 2) suggest that reaction in neat cyclohexene is *entirely* radical and that the ratio of products I, II, and III is determined by the competition among the following reactions of chlorine atom with cyclohexene with the relative rates shown (the values are taken from the high-concentration limits and are not corrected for statistical

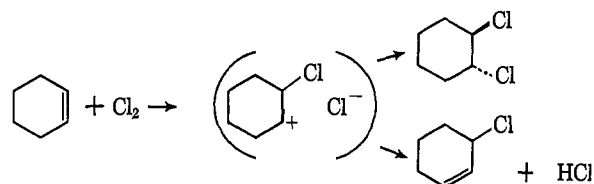


factors). Chain transfer of each of the radicals VII-IX with chlorine produces I-III, respectively, along with a chlorine atom which continues the chain. The 2-chlorocyclohexyl radical VII reacts with chlorine to give >95% the *trans*-1,2-dichloride; this conclusion was also reached from photochlorination studies of chlorocyclohexane in which radical VII was generated by hydrogen abstraction rather than addition.²⁷ For the ionic reaction, observed under oxygen-inhibited conditions, the distribution between I and II can be

(26) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).

(27) G. A. Russell, A. Ito, and R. Konaka, *J. Am. Chem. Soc.*, **85**, 2988 (1963).

taken from curve 17 of Figure 3. The data do not allow us to decide whether the small variation in the ratio of ionic addition to substitution with olefin dilution is an actual function of olefin concentration or, as seems more likely, a function of small medium changes caused by dilution since cyclohexene, cyclohexane, carbon tetrachloride, and trichlorotrifluoroethane, although all "nonpolar," do not have identical polar properties. In view of recent evidence²⁸ of the importance of ion pairs and the nature of the anion in carbonium ion processes even in relatively polar solvents, it seems reasonable that chlorine and cyclohexene react in these nonpolar media to form a tight ion pair consisting of a chlorocarbonium ion (possibly bridged) and a chloride ion, and that this same chloride ion either collapses with the carbonium ion to form I or removes a proton from it to form II. If one then



makes the reasonable assumption that the I/II ratio characteristic of the ionic process will not depend on the nature of the carrier gas, one can determine from eq. 1 the percentage of radical reaction (*r*) at any concentration of olefin for the dark reaction under nitrogen in trichlorotrifluoroethane.

$$\left(\frac{\text{III}}{\text{II}}\right) = \frac{(r)\left(\frac{\text{III}}{\text{I} + \text{II} + \text{III}}\right)_{\text{radical}}}{(r)\left(\frac{\text{II}}{\text{I} + \text{II} + \text{III}}\right)_{\text{radical}} + (1 - r)\left(\frac{\text{II}}{\text{I} + \text{II}}\right)_{\text{ionic}}} \quad (1)$$

where (III/II) is taken from curve 4 of Figure 1,²⁹ (III/(I + II + III))_{radical} = 0.60/(1.95 + 1.00 + 0.60), (II/(I + II + III))_{radical} = 1.00/(1.95 + 1.00 + 0.60), and (II/(I + II))_{ionic} is taken from curve 17 of Figure 3.²⁹ As a check, this calculated value of *r* from eq. 1 can be substituted into eq. 2 to calculate the expected I/II ratio.

$$\left(\frac{\text{I}}{\text{II}}\right) = \frac{(r)\left(\frac{\text{I}}{\text{I} + \text{II} + \text{III}}\right)_{\text{radical}} + (1 - r)\left(\frac{\text{I}}{\text{I} + \text{II}}\right)_{\text{ionic}}}{(r)\left(\frac{\text{II}}{\text{I} + \text{II} + \text{III}}\right)_{\text{radical}} + (1 - r)\left(\frac{\text{II}}{\text{I} + \text{II}}\right)_{\text{ionic}}} \quad (2)$$

where (I/(I + II + III))_{radical} = 1.95/(1.95 + 1.00 + 0.60) and (I/(I + II))_{ionic} is taken from curve 17.²⁹ Values for *r* and (I/II)_{calcd} are shown in Table IV and plotted in Figure 4. It can be seen that *r* approaches zero at infinite dilution; also, the calculated values of I/II agree rather well with the observed values; to this extent the assumption that the radical yield ratio

(28) M. Cocivera and S. Winstein, *ibid.*, **85**, 1702 (1963); D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963); P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).

(29) The values were taken from the "best" curve drawn visually through the experimental points.

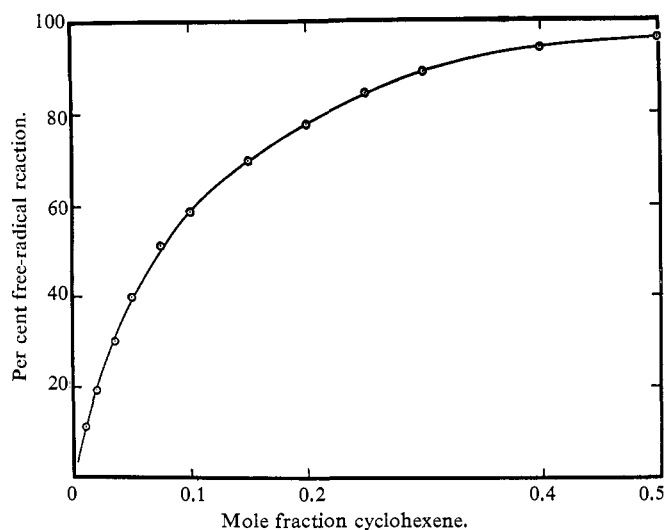


Figure 4. Variation of percentage radical reaction with concentration during chlorination of cyclohexene at 25° in the dark in C₂F₃Cl₃.

(1.95:1.00:0.60) is independent of olefin concentration is confirmed.

Table IV. Dependence of Percentage of Radical Reaction (r) on Cyclohexene Concentration for Chlorination at 25.0° in the Absence of Light and Oxygen

Mole fraction of cyclohexene ^a	r	(I/II) _{calcd}	(I/II) _{obsd} ^b
1.00	(100)		
0.50	97	2.01	1.95
0.30	89	2.11	1.98
0.20	79	2.26	2.11
0.10	60	2.50	2.42
0.050	41	2.72	2.71
0.035	31	2.83	2.82
0.020	20	2.94	2.95
0.010	12	3.02	3.07

^a Diluted with 1,1,2-trichlorotrifluoroethane. ^b From curve 14 of Figure 2.

Kinetic Considerations and Spontaneous Initiation. The radical and ionic processes must have rate laws depending on cyclohexene and/or chlorine with different powers to produce the behavior depicted in Figure 4.³⁰ One can set up the following generalized rate laws for each pathway

$$(dP_R/dt) = k_R(\text{cyclohexene})^p(\text{Cl}_2)^q$$

$$(dP_I/dt) = k_I(\text{cyclohexene})^m(\text{Cl}_2)^n$$

where P_R and P_I represent the radical and ionic products. The experiments summarized in Table I which show that the III/II ratio (and hence r) is not sensitive to the rate of chlorine input, while not completely rigorous since we cannot directly translate a 20-fold change in input rate into a quantitative change in average chlorine concentration,³¹ nevertheless strongly

(30) The failure of the radical-ionic ratio to vary with water concentration, hydrogen chloride concentration, or nature of the reaction vessel suggests that the ionic process can be treated as a simple homogeneous reaction; however, a significant surface reaction apparently can occur on rough glass surfaces.

(31) The rapidity of the reaction makes kinetic study by usual methods impossible; flow techniques would be necessary for a rigorous solution.

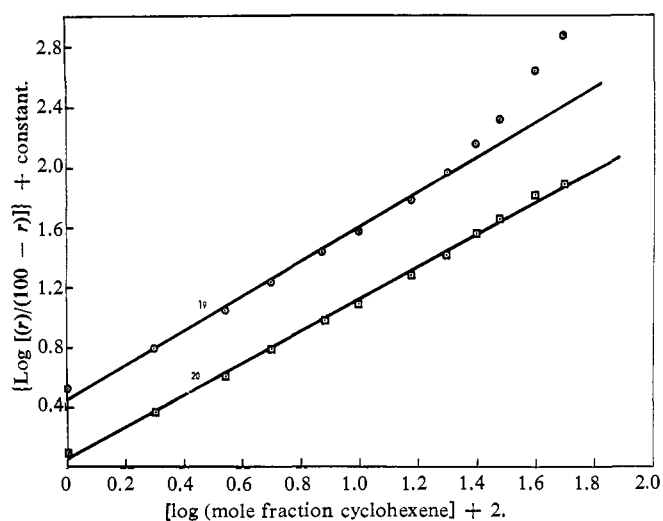


Figure 5. Logarithmic plot of radical-ionic ratio vs. concentration for chlorination of cyclohexene at 25°: ○ (19), based on observed I-II-III ratio of 1.95:1.00:0.60; and □ (20), based on I-II-III ratio of 1.90:1.00:0.64.

suggest that the observed effects of olefin concentration are primarily due to different kinetic orders with respect to cyclohexene rather than chlorine. That is, if $n \neq q$, then $|(p - m)| > |(n - q)|$. If one assumes for the moment that $n = q$, one can write

$$\frac{(dP_R/dt)}{(dP_I/dt)} = \frac{k_R}{k_I}(\text{C}_6\text{H}_{10})^{p-m} \quad (3)$$

If (C₆H₁₀) is essentially constant throughout a run (as it is at low conversion), then

$$\frac{P_R}{P_I} = \frac{k_R}{k_I}(\text{C}_6\text{H}_{10})^{p-m} \quad (4)$$

and

$$\log (P_R/P_I) = \log [(r)/(100 - r)] =$$

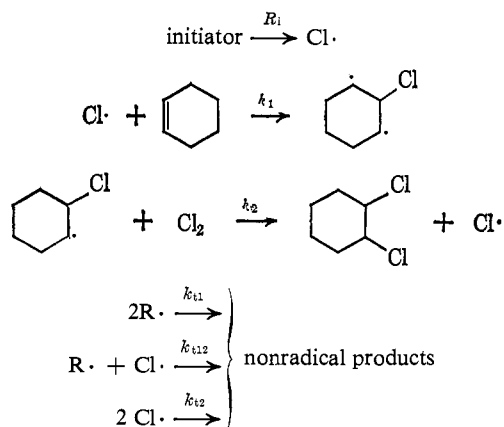
$$\log \frac{k_R}{k_I} + (p - m) \log (\text{C}_6\text{H}_{10}) \quad (5)$$

A plot of $\log [(r)/(100 - r)]$ vs. $\log (\text{C}_6\text{H}_{10})$ is shown in curve 19 of Figure 5. With the assumptions involved, it is encouraging that a reasonably linear portion is obtained between $r = 15$ and $r = 80$. The behavior of the ends of the curve depends strongly on the exact choice of the parameters: $(\text{III}/(\text{I} + \text{II} + \text{III}))_{\text{radical}}$ and $(\text{II}/(\text{I} + \text{II} + \text{III}))_{\text{radical}}$; for example, curve 20 is based on a ratio of I:II:III of 1.90:1.00:0.64 rather than 1.95:1.00:0.60. In either case the slope is 1.1. This admittedly crude treatment suggests that $(p - m)$ is approximately unity.

Although it has been reported³² that chlorination of dilute solutions of cyclohexene in carbon tetrachloride saturated with air and water at 25–35° is second order in chlorine and zero order in cyclohexene (rather than first order in each reactant as observed³² for 2-ethyl-1-hexene and oleic acid), one is forced to question this result since the author reports that no hydrogen chloride was evolved, in contradiction to the present study. Reasonable mechanisms for the ionic reaction are first order in olefin; the radical reaction must then be greater than first order in olefin. The expected chain

(32) G. Roper, *Chem. Eng. Sci.*, 2, 27 (1953).

for the formation of product I is



with analogous propagation steps for formation of II and III. The rate law depends on the relative importance of the various termination steps. Since olefin is present in large excess compared to chlorine, coupling of alkyl radicals seems the more likely.³³ In this case the rate law for formation of radical products is of the form seen in eq. 6. Rather than being of

$$\left(\frac{dP_R}{dt}\right) = \left(\frac{R_i}{2k_{t1}}\right)^{1/2} k_2(\text{Cl}_2) \quad (6)$$

higher order in olefin than a reasonable ionic process, this rate law is not of higher order than *any* ionic process. For the less likely case of termination through chlorine atoms, the rate law is of the form

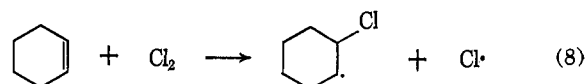
$$\left(\frac{dP_R}{dt}\right) = \left(\frac{R_i}{2k_{t2}}\right)^{1/2} k_1(\text{C}_6\text{H}_{10}) \quad (7)$$

still only first order in olefin whereas a rate law greater than first order in olefin is apparently required.

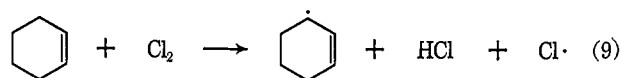
Before an attempt is made to escape this kinetic dilemma, one must consider the nature of the radical initiation process. Since chlorine is stable in alkanes in the dark at 25° (and surely at -78° where the chlorine-cyclohexene radical reaction still proceeds readily), initiation by thermal dissociation of chlorine at the temperatures of this study is impossible. We have shown that addition of suspected peroxidic initiators, hydrogen chloride, and water does not increase the fraction of radical reaction under conditions where the radical and ionic pathways are in active competition. *We therefore propose that initiation is spontaneous; that is, a specific reaction exists between chlorine and cyclohexene which produces free radicals which can initiate chain reactions.*³⁴ By use of available bond energies, approximate enthalpies of reaction for hypothetical interactions involving one molecule each of chlorine and cyclohexene can be calculated (eq. 8 and 9).

(33) However, there may well be gradients of chlorine concentration extending out from the inlet tube because of the rapidity of reaction; if so, the relative importance of the termination steps need not be the same for all parts of the reaction system.

(34) The most convincing proof that initiation is a consequence of the olefin itself and not of impurities or special properties of cyclohexene is that similar behavior has been observed for a variety of olefins and a well-behaved structure-reactivity correlation exists as will be shown in the succeeding paper.³

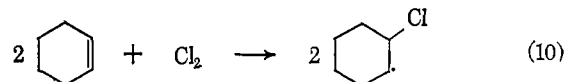


$$\Delta H = D_{\text{Cl-Cl}} + \Delta H_A = (58 - 26) = 32 \text{ kcal./mole}$$

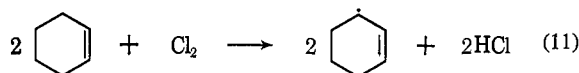


$$\Delta H = D_{\text{Cl-Cl}} + D_{\text{C-H}} - D_{\text{H-Cl}} = (58 + 74 - 103) = 29 \text{ kcal./mole (37 kcal./mole)}^{35b}$$

$D_{\text{Cl-Cl}}$ is the dissociation energy of chlorine molecule^{6c} and ΔH_A is the exothermicity of addition of chlorine atom to ethylene.^{6c,35a} $D_{\text{C-H}}$ is the dissociation energy of the allylic C-H bond of cyclohexene^{35b} and $D_{\text{H-Cl}}$ that of hydrogen chloride.^{6c} Thus the minimum energy of activation for a radical-forming process involving one molecule of each reactant is of the order of 30 kcal./mole, a value surely too great to be of significance at -78°. In fact, we have found that, even at 25°, the stable chlorine-cyclohexane system is not initiated by azobisisobutyronitrile (whose energy of activation for decomposition into radicals is ~31 kcal./mole³⁶) at a rate comparable to the olefin-chlorine reaction. More energetically favorable processes can be devised by use of two molecules of olefin (eq. 10 and 11). Although our



$$\Delta H = D_{\text{Cl-Cl}} + 2\Delta H_A = 58 - 52 = 6 \text{ kcal./mole}$$



$$\Delta H = D_{\text{Cl-Cl}} + 2D_{\text{C-H}} - 2D_{\text{H-Cl}} = (58 + 148 - 206) = 0 \text{ kcal./mole (16 kcal./mole)}^{35b}$$

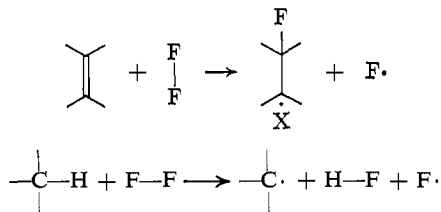
experiments to date give no direct information concerning the details of the initiation process, consideration of over-all energetics favors a process involving at least two molecules of olefin. Returning now to the possible rate laws for the radical reaction (eq. 6 and 7), we see that, in the present interpretation, the rate of initiation, R_i , is a function of cyclohexene concentration and hence the order of the over-all reaction with respect to olefin is increased; spontaneous initiation thus not only explains the source of the observed radical chain reactions but also appears to allow escape from an apparent kinetic dilemma. We are not able, however, to determine at present the exact form of the kinetic equations.

(35) (a) This value is somewhat uncertain since it is based on a rather approximate value for $D_{\text{C}_6\text{H}_9\text{Cl}-\text{Cl}}$; therefore we have not attempted to make any changes in ΔH_A for cyclohexene rather than ethylene in this approximate calculation. (b) We have used 20 kcal./mole as the resonance energy of the allyl radical and subtracted this from 94 kcal./mole, the value for $D_{i-\text{Pr}-\text{H}}$.³⁶ The value of 20 is taken from A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 393; a smaller value (12 kcal./mole) has been suggested by S. W. Benson, A. N. Bose, and P. Nangia, *J. Am. Chem. Soc.*, **85**, 1388 (1963). If the latter value is correct, the over-all enthalpy of hypothetical reactions 9 and 11 will be considerably greater as shown by the values in parentheses.

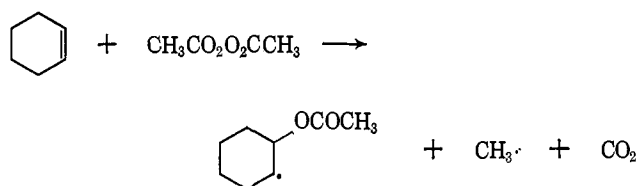
(36) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

This initiation of radical reactions by interaction of chlorine and olefins is surely the explanation of the "induced substitution" observed by Stewart.¹² Similar behavior has been observed recently in the catalysis of butane chlorination by butene or butadiene.³⁷

Such spontaneous initiations by reaction between "even" molecules have been suggested in a number of reactions. The catalysis of radical reactions at Dry Ice temperatures by interaction of organic molecules with small amounts of fluorine has been assumed³⁸ to involve steps such as



More recently Miller and co-workers^{38b} showed that reaction of fluorine and perhaloolefins at -150° leads to mixtures of difluorinated starting materials and difluoro dimers. The formation of radicals of type X is rapid enough to build up a radical concentration at which radical dimerization competes successfully with radical attack on fluorine molecule. Fluorine would be expected to be more favorable than chlorine in such initiation processes since $D_{\text{F-F}}$ is ca. 20 kcal./mole less than $D_{\text{Cl-Cl}}$ ^{6c} whereas $D_{\text{C-F}}$ is ca. 25 kcal./mole greater than $D_{\text{C-Cl}}$.³⁹ Fraenkel and Bartlett⁴⁰ found an unexpectedly rapid reaction between styrene and iodine at 25° , the kinetics of which suggested an initiation step first order in iodine and second order in styrene. Walling^{41a} has found a rapid, radical, dark reaction between *t*-butyl hypochlorite and certain acetylenes. Several authors⁴² have noted that the decomposition of several alkyl hydroperoxides is accelerated by certain olefins even under conditions where induced decomposition has been inhibited. Martin and Drew^{43a} coined the phrase "molecule-induced homolytic decompositions" to describe this type of reaction and reported that decomposition of diacetyl peroxide in cyclohexene at 80° involved at least partially the following reaction. More recently Martin and Koe-



(37) L. M. Kogan and N. P. Ignatova, *J. Gen. Chem. USSR*, **33**, 870 (1963).

(38) (a) W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty, *J. Am. Chem. Soc.*, **78**, 4992 (1956); (b) W. T. Miller, Jr., and S. D. Koch, Jr., *ibid.*, **79**, 3084 (1957); W. T. Miller, Jr., J. O. Stoffer, G. Fuller, and A. C. Currie, *ibid.*, **86**, 51 (1964).

(39) T. Cottrell, "Strengths of Chemical Bonds," 2nd Ed., Butterworth and Co. (Publishers) Ltd., London, 1958, pp. 275, 276.

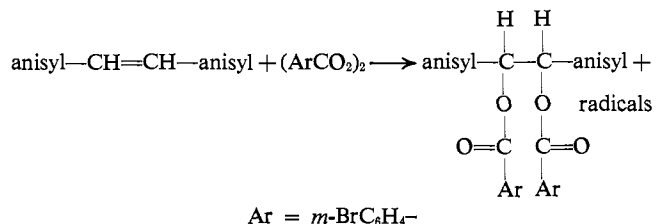
(40) G. Fraenkel and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 5582 (1959).

(41) (a) C. Walling, private communication. (b) The author wishes to acknowledge several helpful discussions with Professor C. Walling concerning these radical-forming reactions.

(42) R. Hiatt, C. W. Gould, and F. R. Mayo, *J. Org. Chem.*, **29**, 3461 (1964); C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 38 (1965), and references therein.

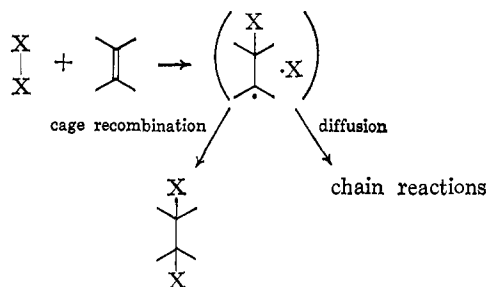
(43) (a) J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1232 (1961); (b) J. C. Martin and T. W. Koenig, *ibid.*, **86**, 1771 (1964).

nig^{43b} have demonstrated by labeling techniques an intramolecular attack of a double bond on a peroxidic linkage during decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate. An apparently similar process has been described by Greene and co-workers⁴⁴ in the reaction of *m,m'*-dibromobenzoyl peroxide with *p,p'*-dimethoxy-*trans*-stilbene which produces both a direct addition product and free radicals which can be



scavenged. Bartlett⁴⁵ has suggested that formation of biradicals best explains the data obtained for 1,2-addition of dichlorodifluoroethylene to dienes. The uncatalyzed thermal polymerization of styrene at 100° involves termolecular initiation, and a reaction of styrene with a styrene dimer to form two radicals has been suggested.⁴⁶ Zutty and Wilson⁴⁷ proposed formation of a biradical by interaction of norbornene and sulfur dioxide as the key step in the almost explosive copolymerization of these monomers at -20° . We feel that the cyclohexene-chlorine reaction represents a facile example of this class of homolytic dissociations.

All these radical-forming processes seem to have a common characteristic in that the energy required to dissociate a bond (the halogen-halogen bond, the O-O bond of peroxides, or the π -bond of dichlorodifluoroethylene) is partially regained by interaction or actual bond formation with an acceptor molecule (the olefin) during homolysis so that a route to dissociation of over-all lower activation energy becomes available. Since such a process would produce two radicals in a cage (except for biradical formation), the actual product observed should depend on the chain length of reactions available. If chain reactions are facile as in



chlorination, the cage recombination product would represent an extremely small fraction of the observed products; however, if no effective chain-reaction path is available, the recombination product could represent a considerable portion of the total product.^{41b} For example, it is difficult to decide whether the direct addition product observed by Greene⁴⁴ is derived from a concerted addition or from cage recombination.

(44) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

(45) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

(46) F. Mayo quoted in R. R. Hiatt and P. D. Bartlett, *ibid.*, **81**, 1149 (1959).

(47) N. L. Zutty and C. W. Wilson, III, *Tetrahedron Letters*, 2181 (1963).

Effects of Complexing Solvents. With this background one can now consider the effects of other solvents investigated. It should be pointed out first that, whereas the number of molecules of ionic product formed is a direct measure of the number of encounters between cyclohexene and chlorine which result in ionic reaction, the number of molecules of radical product represents a mathematical product of those encounters which result in effective homolysis multiplied by the chain length. Since there is no reason to expect the chain lengths in trichlorotrifluoroethane, carbon tetrachloride, and cyclohexane to be identical, the failure of curves 3, 4, and 5 of Figure 1 to coincide exactly is not surprising. Actually, since the nitrogen used was surely not absolutely free from oxygen and therefore some chain inhibition must have occurred, the exact position of the r vs. concentration curve with respect to the axes is not as significant as its curvature. On the other hand, in benzene and carbon disulfide, the decrease in III/II and increase in I/II, which commence as soon as solvent is added and which cannot be counteracted by illumination, appear to be due to solvent effects on the radical reaction. Russell^{22a} and Walling^{22b} have shown that aromatic solvents and carbon disulfide can greatly enhance the selectivity of chlorine atom with respect to tertiary vs. primary hydrogen abstraction reactions; chlorine atom appears to complex with aromatic solvents to form a more discriminating species. The decrease in III/II is reasonable since a more selective radical should have an enhanced preference for allylic attack compared to saturated attack. The concurrent increase in I/II shows that complexing solvents favor addition over allylic substitution in this system. Solvent effects on radical addition of chlorine have recently been demonstrated in a system in which ionic reactions are not a complicating factor.^{22c} The maxima in the I/II curves observed at low olefin concentration (curves 9 and 11 of Figure 2), although surprising at first, are qualitatively in accord with the proposed mechanism of chlorination. As the concentration of complexing solvent increases, the radical portion of the reaction becomes more and more selective and I/II increases; however, at the same time, the ionic reaction upon whose product distribution the solvents have little effect (Figure 3) begins more and more to predominate since the olefin is being diluted; the superposition of these effects predicts passage through a maximum as observed.

Quantitatively, the situation is more complex as illustrated by the following calculation. Assume that: (1) the r vs. olefin concentration curves for the complexing solvents are the same as for the inert solvents (*e.g.*, $r = 20$ at mole fraction cyclohexene = 0.020 in trichlorotrifluoroethane), (2) $(I/II)_{\text{ionic}} \sim 3$ (Figure 3) in all solvents, and (3) $(I/II)_{\text{radical}}$ approaches infinity in complexing solvents (the maximum solvent effect). Then one can calculate that I/II should be ~ 4 at mole fraction cyclohexene = 0.020 in complexing solvents. Since the observed ratio is higher than this in benzene and still higher in carbon disulfide, it appears that assumption 1 is wrong and that r must have increased. Several explanations could be advanced; for example, the chain length may have increased in complexing solvents, or the complexing solvent may be participating

in the initiation process (the gain in energy being the exothermicity of complex formation between chlorine atom and the solvent rather than the exothermicity of addition of chlorine atom to the olefin); we do not have data which permit a decision at this time.

Relative Rates of Chlorine Atom Attack on Cyclohexene. The distribution of products from the radical reaction deserves comment. The ratio of addition to allylic hydrogen abstraction observed in the interaction of free radicals and olefins is known for a number of radicals and a variety of olefins. However, because of the obvious complications in chlorine-olefin reactions, such values are not well known for chlorine atom in solution. The ratio of 1.95 observed for cyclohexene under purely radical conditions shows that abstraction can compete favorably with addition at least in this case. Secondly, the yield of saturated compared to allylic abstraction product is greater than that observed for most radicals. Since the 4-cyclohexenyl hydrogen atom is slightly *deactivated* compared to its saturated counterpart in cyclohexane, no special activating effect of a double bond in a homoallylic position is indicated. Rather, the high III/II ratio appears to be a direct consequence of the highly electrophilic and consequently unselective nature of the chlorine atom. This factor will be considered in more detail in the succeeding paper.³ The ratio of 4-attack to 3-attack observed in reactions of radicals with cyclohexene appears to be diagnostic of the selectivity (and, in a somewhat parallel sense, of the degree of bond breaking in the transition state) of the radical; the percentage of 4-attack decreases from 38% for chlorine atom at 25° to 4.5% for *t*-butoxy radical at 25° to <1% for bromination with N-bromosuccinimide at 78°. ⁴⁸

Experimental

Infrared spectra were determined as 10% carbon disulfide solutions on a Beckman IR-5A instrument; boiling points are uncorrected.

Materials. Cyclohexene (Matheson Coleman and Bell) was refluxed for 2 days over sodium before a center distillation cut was collected daily for use. Cyclohexane was washed well with sulfuric acid, dried, and distilled from sodium. 1,1,2-Trichlorotrifluoroethane, carbon tetrachloride, and carbon disulfide were distilled from Drierite. Benzene was distilled after rejection of the water-containing forerun. Chlorine (Matheson) was passed through sulfuric acid before use; the initial and final one-sixth sections of the cylinder were rejected. Nitrogen (Linde, H. P. Dry) was passed through successive scrubbers containing basic sodium anthraquinone 2-sulfonate-sodium dithionite solution (two scrubbers), lead acetate solution, solid potassium hydroxide and Drierite, and sulfuric acid.⁴⁹ Oxygen (Linde U.S.P.) was passed through sulfuric acid before use.

Reference Compounds. Illumination of a mixture of 80 ml. of cyclohexene and 8.64 g. (0.081 mole) of *t*-

(48) The recent results for NBS brominations of alkylaromatics suggest that the attacking species in these reactions is bromine atom rather than succinimido radical as previously accepted. See C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963); G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963); R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963); and E. Hedaya, R. L. Hinman, and S. Theodoropoulos, *ibid.*, **85**, 3052 (1963).

(49) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 299.

butyl hypochlorite⁵⁰ at 40° under nitrogen with a 275-w. sun lamp until the yellow color had disappeared (45 min.) gave, after removal of solvent and distillation through an 18-in. spinning-band column, a center cut of 40. g. (42%) of 3-chlorocyclohexene (II), b.p. 58° (29 mm.), n^{23D} 1.4881 (lit.⁵¹ b.p. 62° (35 mm.), n^{25D} 1.4860). 1-Chlorocyclohexene (V), b.p. 141–143°, n^{23D} 1.4800 (lit.^{15a} b.p. 141–143°, n^{25D} 1.4780) was prepared from reaction of cyclohexanone with phosphorus pentachloride according to the method of Carroll, *et al.*^{15a} 4-Chlorocyclohexene (III), b.p. 60–61° (43 mm.), n^{23D} 1.4812 (lit.¹⁹ b.p. 88–93° (130 mm.), n^{20D} 1.4822), was prepared by dehydration of 4-chlorocyclohexanol according to the procedure of Birch, *et al.*¹⁹; the 4-chlorocyclohexanol was derived by treatment of 1,4-cyclohexanediol with hydrochloric acid according to the procedure of Owens and Robins.⁵² *cis*-1,2-Dichlorocyclohexane (VI), b.p. 99–100° (30 mm.), n^{24D} 1.4955 (lit.¹⁵ n^{25D} 1.4945) was prepared by treatment of *trans*-2-chlorocyclohexanol (from chlorination of cyclohexene in acetone–water) with thionyl chloride and pyridine.¹⁵

Product Isolation. Chlorine (12 g., 0.17 mole) was condensed in a cold trap and then swept into 100 ml. of cyclohexene illuminated with a 275-w. sun lamp at 6 in. at 25–30° under nitrogen over a 1-hr. period. The reaction mixture was distilled directly through an 18-in. spinning-band column and the following fractions were collected: (1) 1.2 g. (0.01 mole), b.p. 52–55° (29 mm.), n^{24D} 1.4813; g.l.c. (conditions given below) showed predominantly one peak of retention time equal to that of III; the infrared spectrum was consistent with that of authentic III; (2) 5.9 g. (0.05 mole), b.p. 55–56° (29 mm.), n^{24D} 1.4850; g.l.c. showed bands corresponding to approximately equal amounts of II and III and the infrared spectrum contained no bands not present in spectra of II and III; (3) 1.1 g. (0.01 mole), b.p. 40–66° (11 mm.), of a mixture rich in II; and (4) 12.7 g. (0.08 mole), b.p. 66–67° (11 mm.), n^{24D} 1.4891; g.l.c. showed a single peak and the infrared spectrum was consistent with that published^{15b} for *trans*-1,2-dichlorocyclohexane (I) (lit. b.p. 88–89° (30 mm.), n^{20D} 1.4904^{15a}; b.p. 71° (15 mm.), n^{20D} 1.4902^{15b}).

Quantitative Chlorination Runs. A 25-ml., three-necked flask equipped with a reflux condenser and drying tube, a small Teflon stirring bar, and a capillary gas inlet tube was placed in a thermostated bath (25.0 ± 0.1°) equipped with an immovable magnetic stirring motor. After the system was flushed with nitrogen, the appropriate amounts of cyclohexene and solvent were added by calibrated pipet to give a total volume of 15 ml., and the contents were flushed with nitrogen at least 10 min. Chlorine (1.0–1.5 mmoles for all runs reported in Figures 1–4 except down to 0.25 mmole for runs very dilute in cyclohexene) was condensed in a graduated tube surrounded by a Dry Ice–acetone bath; the system was arranged so that this trapping operation was performed entirely under nitrogen. When the reactants were properly flushed, the cold bath was removed and the chlorine

allowed to vaporize into the nitrogen stream flowing toward the reaction vessel; introduction of chlorine required 4–6 min., but could be varied when necessary by placing baths of varying temperature around the chlorine trap. The solution was swept with nitrogen for an additional 5 min. before analysis. The g.l.c. analysis was performed with a Micro-Tek 2500R instrument equipped with 2-m. Perkin-Elmer “R” columns (polypropylene glycol) at a helium flow of 200 ml./min. and inlet temperature of 100° to avoid decomposition of III. The monochlorides were eluted in the order V, IV, III, and II between 15 and 25 min. at 85°, at which temperature no decomposition occurred; the temperature was then programmed to 135° in 5 min. to elute I and VI in that order; total analysis time was 45 min. A thermal conductivity detector was used for early runs but the greater sensitivity of a flame ionization detector was necessary for the dilution studies shown in Figures 1–3 because of the small amounts of chlorine employed to avoid polychlorination. The detector was calibrated with known mixtures and the peak *ratios* shown to be linear over the ranges of concentration and sample size encountered during these runs; occasional recalibration showed that the correction factors used to convert areas to molar quantities were invariant with time. Peak areas were determined either by planimeter or by use of peak height multiplied by retention time; the latter method was as precise as the former (~2% for repeated runs) if the g.l.c. operating conditions were carefully controlled.

Photolysis of Cupric Chloride in Cyclohexene.²⁴ A brown solution of 0.33 g. of cupric chloride and 0.14 g. of lithium chloride in a mixture of 2.5 ml. of cyclohexene and 7.8 ml. of acetonitrile was flushed with nitrogen, sealed, and illuminated with a 275-w. sun lamp at 12 in. at 28° with stirring for 40 hr. The resultant mixture of pale yellow solids in a yellow liquid was washed quickly with three portions of cold water, diluted with carbon tetrachloride, dried, and analyzed by g.l.c. The observed ratio of III/II was 0.55. An identical run gave III/II = 0.70.

Free-Radical Bromination of Cyclohexene. A mixture of 26.7 g. (0.136 mole) of N-bromosuccinimide (NBS), 15.5 ml. (0.155 mole) of cyclohexene, and 100 ml. of carbon tetrachloride was heated under reflux and illuminated with a 275-w. sun lamp at 9 in. for 1 hr. Removal of the solids by filtration and distillation of the filtrate gave 10.7 g. (49%) of 3-bromocyclohexene, b.p. 56° (14 mm.), n^{23D} 1.5297 (lit.⁵³ b.p. 63–64° (15 mm.), n^{25D} 1.5261). G.l.c. of the crude filtrate under the conditions described above except for a column temperature of 95° gave a single band in the time region expected for a C-6 bromide. Treatment of 5 ml. of cyclohexene with 1 ml. of *t*-butyl hypobromite²⁶ at 25° in room light led to rapid decoloration; g.l.c. analysis under identical conditions gave a major band of the same retention time as the product of the NBS reaction along with a minor band (~5%) preceding it.

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