tate and the uncharged bromoacetamide, no long-range electrostatic forces can be involved. It must be concluded that both reagents are being concentrated in the region occupied by the polymer since they are better solvating agents than water. This effect apparently more than compensates for that to be expected due to the concentration of dipolar groups.

Conclusions.—The results of this investigation show that uncharged reagents may react with functional groups of polyelectrolytes at rates differing substantially from those characterizing monofunctional or bifunctional analogs. This phenomenon is probably the result of a concentration of the low molecular weight reagent in the region occupied by the swollen polymer coil. In the poly-(vinylpyridine betaine) reaction this seems to be due to mutual attraction of the hydrophobic residues, while the high reaction rates with poly-(methacrylic acid) appear to be a consequence of a coöperative effect involving interaction of several groups of the polymer with the second reagent. Although this is formally analogous to the presumed principle of enzyme action, it must be emphasized that the enhancement of the reaction rate reported in the present study represents a relatively minor effect.

Acknowledgment.—A constructive criticism of the manuscript by Professor M. L. Bender is gratefully acknowledged.

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

N-Bromosuccinimide. I. Allylic Bromination, a General Survey of Reaction Variables[1-3]

BY HYP J. DAUBEN, JR., AND LAYTON L. MCCOY[4]

RECEIVED DECEMBER 31, 1958

The effect of environmental factors (oxygen, light), reactant impurities (water, hydrogen bromide, bromine, hydroperoxides) and added substances of potential catalytic or inhibitory activity on the course and the relative reaction times of the reaction of N-bromosuccinimide (NBS) with cyclohexene in refluxing carbon tetrachloride has been investigated. Successive removal of reactant impurities and of environmental factors leads to increasingly longer reaction times and ultimately to very slow allylic bromination and increased bromine addition, presumably due to bromine formed by the reaction of NBS with hydrogen bromide eliminated thermally from the allyl bromide product. Initiation of the usual preparative allylic brominations is attributable to allyl hydroperoxides, inadvertently present in the alkene due to prior autoxidation. Comparative reaction times, using cyclohexene with or without its hydroperoxide, for runs with and without added substances have shown that bromanil, picric acid, *s*-trinitrobenzene and iodine function as inhibitors or retarders and that three classes of compounds act as accelerators: (a) known radical generators (azo-bis-isobutyronitrile, benzoyl peroxide, tetralyl and cyclohexenyl hydroperoxides); (b) bromine generators with NBS (bromine, hydrogen bromide, water, ethanol, thiophenol); (c) *t*-amines (triethylamine, pyridine). From effectivity and reactivity orders it is evident that (i) retarders-inhibitors act on the chain-carrying succinimidyl radicals, (ii) known radical sources initiate the reaction by thermal primary dissociation, except for hydroperoxides, which probably also show radical-induced decomposition and oxidation–reduction decomposition with NBS, (iii) bromine, alone or from its congeners, thermally or photochemically yields bromine radicals to catalyze the reaction, and (iv) *t*-amines accelerate the reaction in the absence of peroxides by an oxidation–reduction decomposition reaction with NBS and in the presence of peroxides additionally by an oxidation–reduction decomposition reaction with the hydroperoxide. Definition of the mechanism of action of *t*-amines with NBS provides rational explanation of the earlier antagonistic report (Braude and Waight) of predominant bromine addition to alkenes. In light of new evidence, the mechanism of the allylic bromination reaction must involve different initiation and termination reactions from those proposed by Bloomfield. In its simplest form, initiation results from thermal or photochemical dissociation of initiators to radicals that react with NBS or alkene to produce the propagation radicals, propagation involves a chain reaction of succinimidyl radicals with alkene and of allyl radicals with NBS, the former probably being rate-determining, and termination presumably occurs by the interaction of two succinimidyl radicals to produce not the coupling product, bis-N-succinimidyl, but instead other stable products, possibly succinimide and acryl isocyanate.

Since 1942, when Ziegler and co-workers[5] first reported that N-bromosuccinimide (NBS) could be used to effect allylic brominations of alkenes, many papers concerned with NBS, N-chlorosuccinimide (NCS) and related compounds have been published, and several review articles summarizing these findings have appeared.[6] Most of these publications have dealt with synthetic applications of these reagents. Some have involved studies of certain aspects of the mechanism of side-chain (benzylic) chlorination or bromination,[7] and others have obtained certain results, usually incidental to other objectives,[8] bearing on the mechanism of allylic bromi-

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(1) Presented in part before the 118th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1950 (Abstracts, p. 11-N).

(2) Taken from the Ph.D. Thesis of Layton L. McCoy, University of Washington, 1951.

(3) Supported in part by research contract No. N8-onr-52007 with the Office of Naval Research, U. S. Navy.

(4) Predoctoral Fellow, Atomic Energy Commission, 1950–1951.

(5) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winklemann, *Ann.*, **551**, 80 (1942).

(6) (a) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); (b) W. Ringli, "Bromierungen mit Bromsuccinimid," Leeman, Zurich, 1948; (c) T. D. Waugh, "NBS, Its Reactions and Uses," Boulder, Colo., Arapahoe Chemicals, Inc., 1951; (d) N. P. Buu-Hoi, *Record Chem. Prog.*, **13**, 30 (1952); (e) R. Oda and M. Nomura, *Kagaku*, **8**, 428 (1953); (f) T. Kubota, *ibid.*, **10**, 555 (1955).

(7) (a) J. Adam, R. A. Gosselain and P. Goldfinger, *Bull. soc. chim. Belges*, **65**, 523 (1956); P. Goldfinger, P. A. Gosselain and R. H. Martin, *Nature*, **168**, 30 (1951); M. F. Hebbelynck and R. H. Martin, *Bull. soc. chim. Belges*, **59**, 193 (1950); (b) E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschappen Proc.*, **B56**, 75 (1953); (c) O. O. Orazi, R. A. Corral and E. Colloccia, *Anales asoc. quim. Argentina*, **43**, 55 (1955); O. O. Orazi, N. M. I. Mercere, R. A. Corral and J. Meseri, *ibid.*, **40**, 91 (1952); H. J. Schumacher, O. O. Orazi and R. A. Corral, *ibid.*, **40**, 19 (1952); (d) F. D. Greene, W. A. Remers and J. W. Wilson, THIS JOURNAL, **79**, 1416 (1957); (e) K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

(8) (a) M. G. Ettlinger, Ph.D. Thesis, Harvard University, 1945; *cf.* ref. 6a; (b) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944); (c) H.

nation of alkenes by NBS. The present work is the first of a series of studies on the elucidation of the detailed mechanism of the allylic bromination reaction and it considers the effects of environmental factors and of added substances of potential catalytic and inhibitory action on the course and the reaction time of cyclohexene with NBS in carbon tetrachloride.

Use of cyclohexene as the alkene component and of carbon tetrachloride as reaction medium possesses certain advantages. Cyclohexene is easily purified and symmetrical (formation of isomeric allylic bromides is avoided), reasons which also conditioned its choice in the original Ziegler work. Carbon tetrachloride is the preferred reaction medium for preparative allylic brominations and even though its use results in a largely heterogeneous system, it has the advantages, in addition to simulating the preparative conditions, of providing a constant concentration (saturation) of the brominating agent and a convenient visual assay of the extent of reaction (NBS is more dense, and succinimide less dense, than carbon tetrachloride). The reactant proportions used in all runs (1 mole NBS/1.5 moles cyclohexene/750 ml. carbon tetrachloride/*ca.* 0.01 mole modifier, when added) represents a compromise between manipulative ease and maximum yield of allylic bromide product. To survey the effects of environmental factors and of added substances, a standardized procedure was developed which involved conduct of the reaction at reflux temperature of carbon tetrachloride and determination of the time required for complete reaction by external test (moistened starch–iodide paper) for the disappearance of NBS.

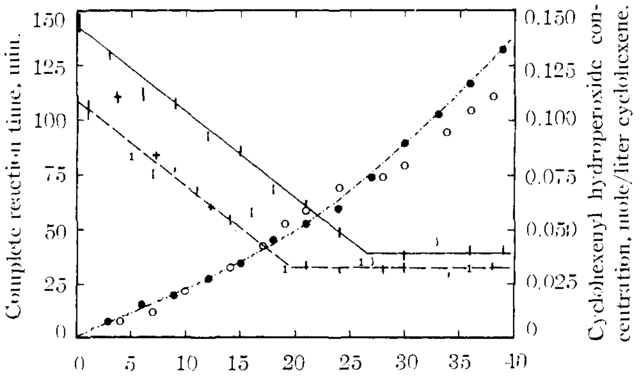

Fig. 1.—Effect of autoxidation of cyclohexene on reaction time with NBS in carbon tetrachloride at 80°; reaction time series 1 (———), series 2 (— —), range for last positive and first negative tests for positive bromine (|), same for series 2 runs made by diluting more concentrated hydroperoxide solutions (+); cyclohexenyl hydroperoxide concentration (— · —), series 1 (●), series 2 (○).

For preparative purposes purification of NBS usually is effected by rapid recrystallization from boiling water, followed by drying in air or over drying agents. Since other workers[9] have reported that NBS purified in this way showed variable activity in preparative benzylic brominations, dependent to a considerable degree on the method of drying, it was necessary to establish the reliability of results obtained with NBS, similarly purified, in allylic brominations. Using the standardized procedure, complete reaction times with cyclohexene were found to be independent of the rate of crystallization but dependent on the drying method employed (air-dried, *ca.* 110 min.; dried over phosphorus pentoxide, *ca.* 165 min.). Air-dried NBS was arbitrarily selected for use in the present study after it had been demonstrated that complete reaction times for each lot of air-dried material in runs with or without added modifiers were reproducible and for different lots, in spite of some variance in absolute values, showed reasonably consistent relative reactivities (ratio of unmodified/modified reaction times).

Different samples of cyclohexene also were found to exhibit different reactivities with NBS and these differences have been shown to be due to the presence of variable amounts of peroxidic impurities. The ease of reaction of atmospheric oxygen with simple non-conjugated alkenes to form allylic hydroperoxides is known to vary considerably with structure, and cyclohexene has been found to be one of the most readily autoxidizable alkenes.[10] In the present work it has been shown that cyclohexene produced a detectable amount of peroxide within one hour after distillation from sodium and storage in a glass-stoppered bottle. When stored in this manner, the peroxide content of the cyclohexene continued to increase steadily for about 100 days, at which time a steady state concentration of about 0.42 *M* peroxide apparently resulted (Fig. 1; peroxide content for only first forty days included).

At regular intervals when the peroxide determinations were made, samples of the aging cyclohexene were removed and reactivity determined under the standardized reaction conditions using a single lot of NBS; repetition of this study with different lots of cyclohexene and NBS gave analogous results, differing only by displacement of the time ordinate due presumably to the slightly different activity of the NBS used (Fig. 1). In both series the reaction times decreased linearly and the peroxide concentrations increased almost linearly up to a peroxide concentration of about 0.035 *M* (in the cyclohexene), but beyond this increased peroxide content failed to decrease the reaction time below a limiting value of about 30 ± 5 min. The insensitivity of the reaction time to increased peroxide concentration beyond about 0.035 *M* apparently is not due to attainment of a steady state concentration of a particular catalytically-active peroxide in the aging cyclohexene; samples of cyclohexene prepared by dilution of material containing high peroxide concentration (>0.035 *M*) with freshly distilled cyclohex-

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Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946); (d) L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 941 (1950); (e) M. C. Ford and W. A. Waters, *ibid.*, 2240 (1952); (f) E. A. Braude and E. S. Waight, *Nature*, **164**, 241 (1949), and *J. Chem. Soc.*, 1116 (1952); (g) W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 525, 689 (1955), and J. Bello, Ph.D. Thesis, Wayne University, 1952; (h) J. C. Martin and P. D. Bartlett, This Journal, **79**, 2533 (1957).

(9) E. Campaigne and W. M. LeSeur, *ibid.*, **70**, 1555 (1948); N. B. Chapman and J. F. A. Williams, *J. Chem. Soc.*, 5044 (1952).

(10) J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949); L. Bateman, *ibid.*, **8**, 147 (1954).

ene gave reaction times which agreed well with those obtained directly from aged samples of the same low peroxide content ($< 0.035\ M$) (Fig. 1). It would appear, at least under these reaction conditions, that peroxide present in excess of about 0.035 M in the cyclohexene, or about 0.006 M in the reactant solution, floods the system and does not contribute additional initiation of the reaction with NBS.[11] The observed dependency of reaction time on peroxide concentration, and particularly the long reaction times at low peroxide concentrations, suggests that some alkenes, which have been reported as unreactive toward NBS or other allylic halogenation agents,[5] may have contained insufficient peroxide, either as the result of too careful purification or of too slow autoxidation, to initiate the reaction.[12] It is also likely, in view of the dependency of reactivity on the purity of the NBS and the alkene, that some of the earlier conclusions about relative reactivity of alkenes also may be invalid.

Environmental Factors.—As usually run for preparative purposes, the reaction of NBS with alkenes is conducted in normal diffuse light and in contact with air (through the condenser). In a few cases a nitrogen atomosphere or precautions to maintain the reaction mixture anhydrous have been employed, but these measures seem to have been used to protect the bromo product from decomposition rather than to change the course or rate of the bromination reaction. Strong light irradiation has been shown to catalyze the reaction of NBS with alkenes[13] and an incandescent bulb placed below the reaction flask frequently has been used to catalyze allylic brominations and to furnish heat needed for refluxing. To determine the effect of diffuse light and of atmospheric oxygen on the course and the time of complete reaction, a series of runs were conducted under various combinations of light-free, oxygen-free and peroxide-free conditions (Table I). The similarity of reaction times for runs 1 and 2, which are carried out under the normal conditions (access to air, preformed peroxides in the cyclohexene) and differed only in the access of diffuse light, indicates that light does not contribute significantly to catalysis of the reaction when peroxides are also present. When preformed peroxides and access of oxygen and moisture are excluded (run 3), the reaction time in diffuse light is almost doubled; when access of light is additionally removed (run 4), reaction occurs very slowly and the reaction time is increased almost ten-fold. The difference between the latter two reaction times indicates that, in the absence of peroxides, even diffuse light may catalyze the allylic bromination reaction.[14] In run 5 it has been shown that a sluggish reaction (run 4 type) may be activated by addition of peroxides that normally would have been present in the reaction mixture. These observations that reaction times become successively longer as peroxides, light and oxygen are eliminated provide convincing evidence of the radical chain nature of the NBS-alkene reaction and of the importance of these catalysts, usually inadvertently present, in synthetic applications of this reaction. The very slow reaction still found when these catalysts are excluded may be attributable to initiation by bromine radicals, formed by thermal homolysis of bromine (*vide infra*) or, possibly, of NBS, or to slow formation of peroxides from residual traces of oxygen not removed by sweeping with nitrogen.

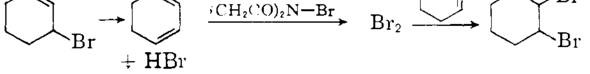
TABLE I

EFFECT OF ENVIRONMENTAL FACTORS ON REACTION OF NBS WITH CYCLOHEXENE IN CARBON TETRACHLORIDE

				Yield, %		
Run	Oxygen[a]	Light	Time, min.	3-Bromocyclohexene	3,6-Dibromocyclohexene	1,2-Dibromocyclohexene
1	+	+	70–75	62	10	1
2	+	–	75–80	60	8[c]	
3	–	+	105–130	55	13	4
4[d]	–	–	>660	40	8	15
5[e]	–	–	305–312	60	2	8
6[f]	–	–	300–360	22	11	37

[a] In runs with an air atmosphere (+) the cyclohexene was 0.022 M in peroxides; in runs with a nitrogen atmosphere (–) the cyclohexene was distilled from sodium in a nitrogen atmosphere directly into the reaction flask. [b] Yields based on major distillation fractions without correction for intermediate fraction. [c] Yield of 3,6-dibromocyclohexene by direct crystallization and isolation; yield of 1,2-dibromocyclohexane not determined. [d] About 6% NBS remained at end of run; all other runs went to completion. [e] Conducted in same manner as run 4 except that after 280 min. 2 ml. of stale cyclohexene (0.022 M in peroxide) was added. [f] Conducted in the same manner as run 4 except that 1 mole per cent. pyridine added initially.

Product analysis of these runs (1–4) clearly indicates that gradual exclusion of environmental catalysts does not alter the fundamental course of the reaction but, by prolonging reaction time, causes a subsequent reaction to become increasingly important. As catalysts are removed and reaction times become longer, the yield of monoallylically brominated product, 3-bromocyclohexene, decreases gradually, the yield of doubly allylically brominated product, 3,6-dibromocyclohexene, remains about constant, and the yield of addition dibromide, 1,2-dibromocyclohexane, increases appreciably. Since it can be shown that 3-bromocyclohexane on continued refluxing in carbon tetrachloride, conditions comparable to those encountered in slow runs, undergoes slow dehydrobromination (*ca.* 1%/hr.), decreased yields of 3-bromocyclohexene at the expense of increased yields of 1,2-dibromocyclohexane are readily explained by the reactions



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[11] The heterogeneous reaction conditions employed in this study may be responsible for the observed limiting reaction time. Due to the low solubility of NBS in carbon tetrachloride, reaction time will be dependent on peroxide concentration up to the point where the NBS is consumed as fast as it dissolves and beyond this additional peroxide can initiate only other reactions.

[12] Evidence presented later in this study and from subsequent kinetic studies [(a) E. A. Youngman, Ph.D. Thesis, University of Washington, 1952] establish that peroxides or other sources of radical initiators are necessary for allylic bromination of cyclohexene, and presumably other alkenes, by NBS. Other studies [(b) H. G. Booker, M. Sc. Thesis, University of Washington, 1955] have shown that different N-bromoimides (NBS, N-bromoglutarimide, N-bromodimethylhydantoin and N-bromophthalimide) require different amounts of peroxides or other initiators to effect allylic bromination of cyclohexene.

[13] C. Meystre, L. Ehmann, R. Neber and K. Miescher, *Helv. Chim. Acta*, **28**, 1252 (1945).

[14] Similar catalysis by light has been observed in benzylic brominations of toluenes by NBS and by dibromodimethylhydantoin in carbon tetrachloride.[7c]

Similar decompositions of allylic bromides have been reported previously and in certain cases conjugated dienes have been isolated as products from allylic brominations as the result of spontaneous dehydrobromination during conduct of the substitution reaction.[15]

Effect of Modifiers.—Prior to the present study relatively little was known about the effect of added substances on the rate and the course of the reaction of alkenes with NBS. Ettlinger[8a] had shown that the decomposition of NBS in dioxane was accelerated by dioxane peroxide or amines and was retarded by bromanil. Schmid and Karrer[8c] had demonstrated that benzoyl peroxide was an effective catalyst for allylic bromination of alkenes by NBS, and Büchi, Seitz and Jeger[16] had used suspended barium carbonate to prevent excessive dehydrobromination of the allylic bromide product during the reaction. Subsequent to the present work, Ford and Waters[8e] showed that allylic and benzylic brominations by NBS were accelerated by azo-bis-α-methyl-butyronitrile or dimethyl azo-bis-isobutyrate and were retarded by iodine or chloranil. Braude and Waight[8f] have found that *t*-amines, tertiary and quaternary ammonium halides, and inorganic halides alter the course of reaction of alkenes with NBS in chloroform to give predominantly bromine addition products; Bailey and Bello[8g] obtained similar results when inorganic halides were added.

In the present study the effect of over twenty modifiers (potential accelerators or retarders) on the time required for complete reaction of NBS with cyclohexene in carbon tetrachloride under standardized conditions has been investigated. The majority of these studies have been made using cyclohexene containing 0.022 *M* peroxide; the presence of peroxide assured more consistent reaction times and this concentration of peroxide, which corresponds to a point on the slanting (peroxide-dependent) portion of the curve in Fig. 1, enabled comparative studies of both accelerating and retarding modifiers on the same reaction system. A limited number of studies were conducted using peroxide-free cyclohexene and with the cyclohexene containing 0.088 *M* peroxide, which corresponds to a point on the limiting portion of the curve in Fig. 1; in all cases the modifiers were present in about 1 mole per cent. concentration relative to NBS. The results obtained, expressed as relative reactivities (reaction time for unmodified (control) run/reaction time for modified run), are summarized in Table II.

TABLE II

EFFECT OF ONE MOLE PER CENT. MODIFIER ON REACTION TIME OF NBS WITH CYCLOHEXENE

Modifier[b]	Relative reactivity[a] Peroxide concn. in cyclohexene 0.000 *M*	0.022 *M*	0.088 *M*
Triethylamine	4.2–4.8	7.9–9.9	1.9–2.4
Azo-bis-isobutyronitrile[c]	6.0–7.3	4.8–6.6	0.92–1.1
Pyridine	2.8–3.2	3.6–4.8	2.4
Benzoyl peroxide		2.8–5.9	
Tetralyl hydroperoxide[d]	4.6–4.9	2.4–5.6[l]	1.1–1.3
Bromine	2.4–2.6	3.3–4.4	1.1
Thiophenol[e]		2.7–2.9	
Water		*ca.* 1–4[m]	
Ethanol		1.6–2.4	
Hydrogen bromide		1.8–2.1	
Piperidine[f]		1.0–1.6	
Succinimide[g]		1.1	
Di-*t*-butyl peroxide[h]		0.97–1.4	
Magnesium oxide		.92–1.2	
Hydroquinone	0.25–0.46	.57–1.0	1.1–1.2
m-Dinitrobenzene		.59–0.84	
Iodine		.47– .58	
Tetrabromohydroquinone[i]		.19– .69	
s-Trinitrobenzene	0.25–0.35	.37– .52	0.21–0.92
Bromanil[j]	0.15	0.33	0.18
Picric acid[k]		0.31	

[a] Relative reactivity = time for complete reaction without modifier/time for complete reaction with modifier, both containing stated peroxide concentration (moles liter^{-1}) in the cyclohexene used. [b] All modifiers used at a concentration of about 1 mole per cent., relative to NBS; unless otherwise indicated modifiers were Eastman white label or comparable grade and were used without purification. [c] Prepared by the method of J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896), m.p. 101–102°. [d] Prepared by E. A. Youngman by the method of H. Hock and W. Susemühl, *Ber.*, **66**, 61 (1933), m.p. 56°, 99.9% peroxide content. [e] Purified by B. S. Baldwin by fractional distillation under reduced pressure from zinc dust in a nitrogen atmosphere just before use. [f] Middle fraction of distilled Eastman practical grade material, b.p. 106°. [g] Technical grade sample recrystallized from 95% ethanol to constant m.p. 125–126°. [h] Sample supplied by Shell Development Co. [i] Prepared by E. A. Youngman by the method of A. R. Ling, *J. Chem. Soc.*, **61**, 558 (1892). [j] Prepared by the same method, m.p. 295–296° dec. [k] Eastman white label sample containing 15% water was dried at 80° (20 mm.) over phosphorus pentoxide for 24 hours and then recrystallized from anhydrous benzene. [l] Relative reactivity of 0.5 mole per cent. tetralyl hydroperoxide plus 0.75 mole per cent. pyridine was 7.9–9.2. [m] Results were erratic and irreproducible, being more dependent on the fineness of dispersion than on the amount of water.

In runs using cyclohexene containing 0.022 *M* peroxide, the relative order of effectiveness of retarders was found to be: bromanil (tetrabromo-*p*-benzoquinone), picric acid > *s*-trinitrobenzene ⋗ iodine > *m*-dinitrobenzene > hydroquinone; tetrabromohydroquinone also functions as a retarder but the inconsistent results obtained preclude assignment of its position in this series. The erratic behavior shown by both hydroquinone and tetrabromohydroquinone may be attributable to their low solubility in carbon tetrachloride but, more likely, is due to their oxidation by traces of oxygen to soluble strongly retarding quinones. At this peroxide concentration hydroquinone is only a weak retarder (increases reaction time less than twofold), iodine, di- and trinitrobenzene are more effective retarders (reaction times approximately doubled), but bromanil and picric acid are found to be, at least, moderately strong retarders (reaction times increased threefold or more). Additional support for these conclusions about the effectiveness of retarders derives from the observations that the relative reactivities of runs with bromanil or *s*-trinitrobenzene are essentially independent of the peroxide concentration but with hydroquinone the relative effectiveness decreases steadily as the peroxide concentra-

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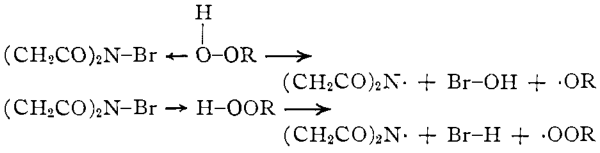
(15) C. Meystre, H. Frey, A. Wettstein and K. Miescher, *Helv. Chim. Acta*, **27**, 1815 (1944); P. Karrer and J. Ritschmann, *ibid.*, **28**, 793 (1945).

(16) G. Büchi, K. Seitz and O. Jeger, *ibid.*, **32**, 39 (1949).

tion is increased, no retarder action being found at the highest peroxide concentration.[17] Qualitative results indicate that sulfur acts as a retarder and certain observations suggest that oxygen functions as a retarder or inhibitor.[18]

The order of effectiveness of retarders on the allylic bromination reaction is found to be completely discordant with inhibitor–retarder order for autoxidations (phenols, aromatic amines $\gg$ chloranil, trinitrobenzene)[19] but to be in excellent agreement with the inhibitor–retarder order for induced decomposition of benzoyl peroxide or for polymerization of vinyl acetate, styrene and methyl methacrylate (more reactive quinones, picric acid $>$ trinitrobenzene $>$ *m*-dinitrobenzene $>$ hydroquinone).[20] Since effectiveness of these inhibitor-retarders in polymerizations decreases as the electron-accepting properties of the polymer radicals increase,[20c,21] the relatively low retarding action of these modifiers in the allylic bromination reaction indicates that the retarders react with the electron-accepting chain carriers, succinimidyl radicals, rather than with the electron-donating cyclohexenyl radicals. This conclusion is in accord with the findings of Kooyman, Van Helden and Bickel[7b] that benzylic bromination of substituted toluenes by NBS is facilitated by electron-donating substituents and retarded by electron-accepting ones ($\rho = -1.55$).

Almost half of the modifiers examined (Table II) proved to be accelerators for the allylic bromination of cyclohexene by NBS. The accelerators may be divided into three groups: (i) normal initiators of radical reactions (azo-bis-isobutyronitrile, benzoyl peroxide, tetralyl hydroperoxide, cyclohexenyl hydroperoxide, di-*t*-butyl peroxide), (ii) bromine-producing group (bromine, hydrogen bromide, ethanol, water, thiophenol) and (iii) amine group (triethylamine, pyridine, piperidine). For the normal initiator group the accelerator order in runs using cyclohexene containing 0.022 *M* peroxide was found to be: azo-bis-isobutyronitrile $>$ benzoyl peroxide $>$ tetralyl hydroperoxide $>$ di-*t*-butyl peroxide[22]; at an equivalent concentration (0.0148 moles/liter reactant solution) cyclohexenyl hydroperoxide was about as effective as azo-bis-isobutyronitrile. With the exception of the hydroperoxides, the accelerator order for the other members of this group parallels their estimated rates of primary decomposition,[23] as expected for initiators subject to little or no induced decomposition. Hydroperoxides, on the other hand, are known to be very susceptible to induced decomposition not only by radicals[23c,24] but also by donor or acceptor molecules[23d] and the relatively greater accelerator action of cyclohexenyl and tetralyl hydroperoxides in the NBS allylic bromination reaction undoubtedly arises from such induced decompositions. In fact, certain observations by others[23d,24c] and favorable energetics make it very probable that NBS is particularly effective in promoting induced decomposition of hydroperoxides by one or both of the following bimolecular reactions, the first being energetically more favorable. Pronounced acceleration of the allylic bromination reaction is also observed when peroxide-free cyclohexene is used; azo-bis-isobutyronitrile and cyclohexenyl hydroperoxide are about equally active (both give limiting reaction times) and more effective than tetralyl hydroperoxide. When cyclohexene containing 0.088 *M* peroxide was used, neither azo-bis-isobutyronitrile nor tetralyl hydroperoxide produced significant additional acceleration, presumably because limiting reaction times had already been attained by the high concentration of cyclohexenyl hydroperoxide present.



$$(CH_2CO)_2N{-}Br \leftarrow \overset{\displaystyle H\atop|}{O}{-}OR \longrightarrow (CH_2CO)_2N\cdot + Br{-}OH + \cdot OR$$

$$(CH_2CO)_2N{-}Br \rightarrow H{-}OOR \longrightarrow (CH_2CO)_2N\cdot + Br{-}H + \cdot OOR$$

The second group of accelerators is composed of bromine and its congeners, hydrogen bromide, ethanol, water and thiophenol.[25] Hydrogen bromide reacts rapidly with NBS to produce bromine, and oxidation of other accelerators in this group by NBS yields hydrogen bromide and, consequently, bromine.[26] Bromine functions as an effective accelera-

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[17] The procedure used in the present study does not allow distinction to be made between inhibitor and retarder action of the modifiers. However, the fact that runs with trinitrobenzene and modifiers below it in the series were all found to go to completion suggests that these modifiers are acting only as retarders. On the other hand, all runs with bromanil or picric acid present were incomplete even after lengthy reaction times (in the longest run, with bromanil and no added peroxide, little succinimide had formed even after 11 hours) and, accordingly, these two modifiers may have functioned as true inhibitors.

[18] In a run using cyclohexene artificially aged by passage of oxygen through it for a few minutes and followed by several days standing, the reaction time was shortened appreciably when the aged cyclohexene sample was "deoxygenated" by passage of nitrogen through it for an hour. Kinetic studies[12a] have shown that traces of oxygen effectively inhibit the initiated allylic bromination reaction at low NBS concentrations and that consistent results are obtained only when reactants have been thoroughly degassed.

[19] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3233, 3238 (1955).

[20] (a) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946); (b) P. D. Bartlett and H. Kwart, *ibid.*, **72**, 1051 (1950) (value for picric acid quoted in ref. 21, p. 174); (c) J. L. Kice, *ibid.*, **76**, 6274 (1954); (d) R. L. Frank and C. E. Adams, *ibid.*, **68**, 908 (1946); (e) S. G. Foord, *J. Chem. Soc.*, 48 (1940).

[21] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 168.

[22] The full magnitude of acceleration by azo-bis-isobutyronitrile or benzoyl peroxide may not be shown in the NBS reaction run under the present conditions because their reaction times are close to the limiting values; *cf.* ref. 11.

[23]

	$k(1st)_d$, 80°, sec.$^{-1}$	Half-life hr.
Azo-bis-isobutyronitrile[a]	1.60×10^{-4}	1.21
Benzoyl peroxide[b]	3.28×10^{-5}	5.87
Tetralyl hydroperoxide[c]	1.37×10^{-7}	1410
Cyclohexenyl hydroperoxide[d]	*ca.* 1×10^{-7}	*ca.* 2000
Di-*t*-butyl peroxide[e]	2.9×10^{-7}	6700

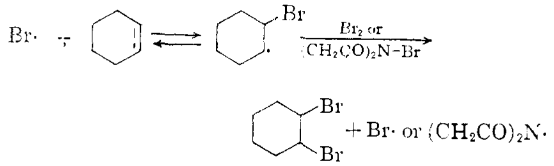
Primary decomposition rates at 80° are available or estimatible from data in the following references: [a] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949); [b] ref. 20a; [c] J. R. Thomas, *ibid.*, **77**, 246 (1955); [d] L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952); *cf.* ref. 23c; [e] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948).

[24] (a) V. Stannett and R. B. Mesrobian, *ibid.*, **72**, 4125 (1950); (b) F. H. Seubold, Jr., F. F. Rust and W. E. Vaughan, *ibid.*, **73**, 18 (1951); (c) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 492 (1947), and 1574, 1578 (1948).

[25] A similar accelerating effect of bromine has been observed in the benzylic bromination of toluene by 1,3-dibromo-5,5-dimethylhydantoin.[7c]

[26] C. A. Grob and H. U. Schmidt, *Experientia*, **5**, 199 (1949), have shown that benzyl alcohol is oxidized by NBS in carbon tetrachloride to benzaldehyde.

tor of allylic bromination both in the absence and the presence of cyclohexenyl hydroperoxide; its accelerating effect is somewhat greater in the presence of low peroxide concentration but limiting reaction times obscure any acceleration at high peroxide concentration. Under these reaction conditions, refluxing carbon tetrachloride and diffuse daylight, bromine radicals would be produced by the thermal or photochemical homolysis of bromine[27a] and be able to initiate allylic bromination[8b,28] either directly or indirectly. Direct initiation would result by displacement of bromine radical on an allylic hydrogen of cyclohexene or on the bromine of NBS to form chain-carrying cyclohexenyl or succinimidyl radicals. Since radical-chain addition of bromine to an alkene is incomplete and reversible,[27a] the intermediate bromocyclohexyl radical could cause indirect initiation either by reversal to form a bromine radical or by displacement on bromine or NBS to yield the same chain-carrying radicals.



The greater acceleration produced by bromine in the presence of peroxides may be due to a bromine radical-induced decomposition of the hydroperoxide or to a bimolecular homolytic reaction between hydroperoxide and bromine molecules. The lesser acceleration shown by other members of this group (bromine > thiophenol > ethanol, hydrogen bromide; water shows variable results) would seem to be determined largely by the efficiency of their reaction with NBS to form bromine or by experimental difficulties; with hydrogen bromide low solubility in carbon tetrachloride results in losses and with water acceleration appeared to be more dependent on degree of dispersal in the solvent than on amount. Product analysis has demonstrated that use of hydrogen bromide as an accelerator does not alter the fundamental course of the allylic substitution reaction since product composition, when corrected for the 1,2-dibromocyclohexane expected from the addition of bromine formed by the reaction of the hydrogen bromide with NBS, proved to be very similar to those formed when cyclohexenyl hydroperoxide, azo-bis-isobutyronitrile or benzoyl peroxide were used as initiators (Table III).

$$\mathrm{ROOH} + \mathrm{Br}\cdot \longrightarrow \mathrm{RO}\cdot + \mathrm{HOBr}$$

$$\mathrm{ROOH} + \mathrm{Br_2} \longrightarrow \mathrm{RO}\cdot + \mathrm{HOBr} + \mathrm{Br}\cdot$$

TABLE III

EFFECT OF ACCELERATORS ON PRODUCT COMPOSITION FROM REACTION OF NBS WITH CYCLOHEXENE[a]

Accelerator	Product yield,[b] % Monobromide	Dibromides
None	62	11
Azo-bis-isobutyronitrile	65	10
Benzoyl peroxide	64	12
Hydrogen bromide	58 (55)[c]	7.5 (20.0)[c]
Piperidine	59	6
Pyridine	60	10
Triethylamine[a]	56	10
Water (finely dispersed)	59	14

[a] Cyclohexene used was 0.022 *M* in peroxides except in triethylamine run when freshly distilled (peroxide-free) cyclohexene was used. [b] Monobromide = 3-bromocyclohexene, Dibromides = 3,6-dibromocyclohexene + 1,2-dibromocyclohexane; intermediate distillation fractions not included in these yields. [c] Parenthetical values are observed values which were corrected by assuming complete reaction of the hydrogen bromide with NBS to give bromine and subsequently 1,2-dibromocyclohexane. The initial amount of hydrogen bromide in the carbon tetrachloride was about 6 mole per cent., but due to its insolubility in this solvent an appreciable amount was lost before reaction began and, therefore, the actual yields lie somewhere between these extremes.

In contrast to the acceleration shown by bromine, iodine has been found to be a moderately effective retarder of the allylic bromination reaction.[29] This striking difference between the action of the two halogens fundamentally derives from the fact that bonds to iodine atoms are consistently weaker than the corresponding bonds to bromine atoms. Due to the easier homolysis of iodine molecules and the lower additive and abstractive reactivity of iodine atoms toward alkenes,[27b,c] iodine atoms tend to accumulate and thereby retard the reaction by coupling with the chain-carrying succinimidyl and cyclohexenyl radicals. Subsequent slow dissociation of the coupling products, N-iodosuccinimide[30] and cyclohexenyl iodide, may occur but the net effect will be retardation due to lessening of the number or the length of the chain reactions.

Prior to the present work it had not been observed that *t*-amines are effective accelerators of the allylic bromination of alkenes by NBS. It had been shown, however, by Ettlinger[8a] that NBS is decomposed violently by tri-*n*-butylamine and Colegrove and Waters[31] had obtained some evidence that triethylamine, N,N-dimethylaniline and N-methylpiperidine in carbon tetrachloride undergo oxidative dealkylation on reaction with NBS. On the other hand, Braude and Waight[8f] had shown that triethylamine, as well as triethylammonium and tetraethylammonium halides, at concentration levels of 10-40 mole per cent. changed the course of the reaction of NBS with cyclohexene in chloroform or petroleum ether from predominant allylic substitution to predominant bromine addition. Consequently, it was surprising to discover that under the usual reaction conditions the addition of smaller quantities of triethylamine or pyridine produced marked acceleration of the allylic bromination reaction; piperidine showed little or no acceleration, possibly because of its conversion to N-bromopiperidine by

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(27) (a) F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940); (b) H. Steinmetz and R. M. Noyes, THIS JOURNAL, **74**, 4141 (1952); (c) R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

(28) H. Schaltegger, *Helv. Chim. Acta*, **33**, 2101 (1950), has shown that photochemically-produced bromine radicals, formed by irradiation of very dilute bromine solutions, initiate allylic bromination of certain steroidal alkenes.

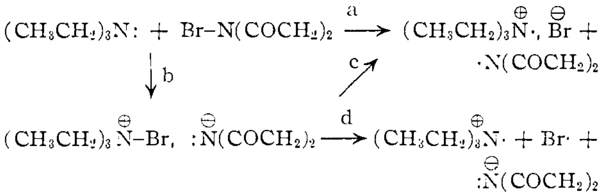
(29) Ford and Waters[8c] have found that iodine exerts a moderate retarder action on the benzylic bromination of toluene by NBS initiated by dimethyl azo-bis-α-methylbutyrate. Hebbelynck and Martin[7a] have reported that iodine failed to retard the light-catalyzed benzylic chlorination of toluene by NCS.

(30) C. Djerassi and C. T. Lenk, THIS JOURNAL, **75**, 3493 (1953), have reported that N-iodosuccinimide shows "no free radical activity" when refluxed with toluene in carbon tetrachloride in the presence of benzoyl peroxide and strong light.

(31) S. L. Colegrove and W. A. Waters, *J. Chem. Soc.*, 907 (1940).

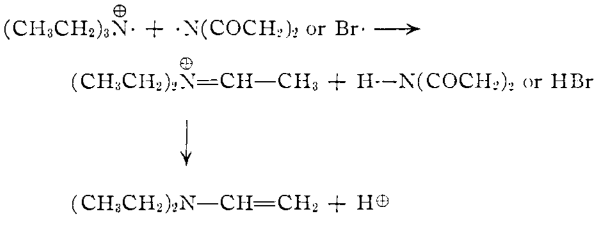
NBS[32] (Table II). Furthermore, in runs with these three amine modifiers product compositions were virtually the same as those obtained when other types of accelerators were used (Table III). Acceleration by amines is shown both in the absence and in the presence of peroxides, but their relative effectiveness varies with peroxide concentration. With peroxide-free cyclohexene, the *t*-amines are less effective than azo-bis-isobutyronitrile or tetralyl hydroperoxide (azo-bis-isobutyronitrile > tetralyl hydroperoxide > triethylamine > pyridine > bromine) but with cyclohexene containing 0.022 *M* peroxide triethylamine excels all others and pyridine becomes as active as benzoyl peroxide (triethylamine > azo-bis-isobutyronitrile > pyridine $\geqslant$ benzoyl peroxide > bromine > tetralyl hydroperoxide). Triethylamine and pyridine are unique in that they are the only modifiers found to produce acceleration when cyclohexene containing 0.088 *M* peroxide was used; in view of the explanation of the limiting reaction times advanced earlier,[11] it would appear that this unique acceleration by *t*-amines at high peroxide concentration may be due to their ability to increase the solubility or rate of solution of NBS in the reaction medium.

Acceleration of the allylic bromination reaction by *t*-amines very likely arises from two sources: (i) amine-induced homolytic decomposition of NBS, and (ii) amine-induced homolytic decomposition of the hydroperoxide. Several lines of evidence strongly support the contention that *t*-amines react with NBS by one or more of the following oxidation–reduction-displacement mechanisms (a, b + c, b + d). Energy considerations indicate that such oxidation–reduction-decomposition reactions are



$$\begin{tikzcd}[column sep=small]
(CH_3CH_2)_3N: + Br\text{-}N(COCH_2)_2 \arrow[r, "a"] \arrow[d, "b"] & (CH_3CH_2)_3\overset{\oplus}{N}\cdot,\ \overset{\ominus}{Br} + \cdot N(COCH_2)_2 \\
(CH_3CH_2)_3\overset{\oplus}{N}\text{-}Br,\ :\overset{\ominus}{N}(COCH_2)_2 \arrow[ur, "c"] \arrow[r, "d"] & (CH_3CH_2)_3\overset{\oplus}{N}\cdot + Br\cdot + :\overset{\ominus}{N}(COCH_2)_2
\end{tikzcd}$$

feasible, the low ionization potentials of *t*-amines being particularly important in facilitating these reactions.[33] An analogous one-step oxidation–reduction-displacement reaction of dimethylaniline or pyridine on tris-*p*-nitrophenylmethyl bromide to form the corresponding trityl radical has been suggested by Leffler,[34a] and Horner and co-workers[34b] have obtained convincing evidence that dimethylaniline (and probably most *t*-amines except pyridine) react with benzoyl peroxide by the two-step mechanism to give initially $C_6H_5\overset{\oplus}{N}(CH_3)_2$—OOC—$C_6H_5$, $^{\ominus}OOCC_6H_5$ which then undergoes homolysis to $C_6H_5\overset{\cdot\oplus}{N}(CH_3)_2$ and $\cdot OOCC_6H_5$. Furthermore, these oxidation-reduction-displacement reactions provide cogent explanation of the formation of enamine products from the action of NBS on triethylamine and other suitable *t*-amines[35] by incorporating the subsequent homolytic elimination step



$$(CH_3CH_2)_3\overset{\oplus}{N}\cdot + \cdot N(COCH_2)_2 \text{ or } Br\cdot \longrightarrow$$
$$(CH_3CH_2)_2\overset{\oplus}{N}{=}CH{-}CH_3 + H{-}N(COCH_2)_2 \text{ or } HBr$$
$$\downarrow$$
$$(CH_3CH_2)_2N{-}CH{=}CH_2 + H^{\oplus}$$

With this new knowledge about the reaction of *t*-amines with NBS, explanation of the different results obtained by Braude and Waight and in the present work becomes possible. As pointed out by Dunstan and Henbest[35] Braude and Waight's reaction of NBS with triethylamine in the absence of cyclohexene proceeded according to the stoichiometrical equation, 2 $(CH_3CH_2)_3N$ + 1 NBS → 1 $(CH_3CH_2)_2NCH{=}CH_2$ + 1 $(CH_3CH_2)_3\overset{\oplus}{N}H$, $Br^{\ominus}$ + 1 $HN(COCH_2)_2$, and our findings indicate that it probably occurred *via* radical intermediates. Moreover, in their study of the effect of triethylamine on the reaction of NBS with cyclohexene, Braude and Waight added NBS to a chloroform solution of the amine and only after the ensuing reaction was complete was the cyclohexene added. Consequently, by this technique the radicals formed in the rapid oxidation–reduction-displacement reaction of amine with NBS were consumed in the production of diethylvinylamine, triethylammonium bromide and succinimide before the cyclohexene was added, and the course of the reaction of NBS with cyclohexene was altered only to the extent that the triethylammonium bromide reacts with NBS to form bromine and, ultimately, 1,2-dibromocyclohexane. The high yields of dibromide products obtained when tri- or tetraalkylammonium halides[8f] (or inorganic halides[8f,g]) are added may be explicable in the same manner or be due to a surface catalytic action that induces bromine addition by a polar mechanism, as previously suggested.[8f,g] The technique used in the present work differed in that amine modifier was added to the mixture of NBS and cyclohexene so that the radicals from the amine–NBS reaction were utilized as formed to initiate the allylic bromination reaction; the use of smaller amounts of amine in our work (1 *vs.* 10 mole per cent.) also con-

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[32] A. Hofmann and F. Troxler, U. S. Patent 2,516,002 (1950), have found that certain *sec*-amines undergo N-bromination by NBS.

[33] The heat of reaction a (or b + c) would be: $\Delta H = D(Br\text{-}N(COCH_2)_2) + IP((CH_3CH_2)_3N) - EA(Br\cdot) - E_{\text{ion pair}} - E_{\text{solvation}}$. Values for the ionization potential of triethylamine (173 kcal. mole^{-1}; K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 542, 1773 (1953)) and the electron affinity of bromine atom (81.6 kcal. mole^{-1}; H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953)) are known and the bond dissociation energy of NBS has been estimated to be about 44 kcal. mole^{-1} [12a]; with these values, $\Delta H = 135 - E_{\text{ion pair}} - E_{\text{solvation}}$. Approximating as Coulombic attraction, ion pair energy would be about 141 kcal. mole^{-1} at 3 Å. and about 94 kcal. mole^{-1} at 4 Å., reasonable limits for the interionic distance. With allowance for solvation energy and for the verticality of the ionization potential, it follows that the reaction should be exothermic. Pyridine, due to its higher ionization potential, would be expected to show lesser tendency to undergo oxidation–reduction-displacement reactions.

[34] (a) J. E. Leffler, THIS JOURNAL, **75**, 3598 (1953); (b) L. Horner and E. Schwenk, *Angew. Chem.*, **61**, 411 (1949), L. Horner and H. Junkermann, *Ann.*, **591**, 53 (1955), and intervening papers in this series.

[35] D. Buckley, S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4901, 4905 (1957), proposed that the reaction of NBS with triethylamine involved initial complex formation followed by heterolytic elimination to give the enamine conjugate acid but did consider the possibility that the analogous reaction of chloranil with *t*-amines occurred by a radical mechanism.

tributed to lower yields of the addition dibromide product.[36]

The greater acceleration of the allylic bromination reaction by *t*-amines in the presence of cyclohexenyl hydroperoxide than in its absence would appear to indicate that *t*-amines also can effect an oxidation–reduction-displacement reaction on hydroperoxides.[37] In spite of the fact that amine-induced decompositions of diacyl peroxides has been

$$\mathrm{RO{-}OH} + :\mathrm{N(CH_2CH_3)_3} \longrightarrow \mathrm{RO}\cdot + \mathrm{OH}^{\ominus} + \cdot\overset{\oplus}{\mathrm{N}}\mathrm{(CH_2CH_3)_3}$$

studied extensively,[34b] very few amine-induced decompositions of hydroperoxides have been reported previously.[38] The same accelerator order (triethylamine > pyridine) is found for allylic brominations in the absence or presence of hydroperoxides, as expected if relative ionization potentials are the major determining factor. Limited product composition data suggest that this interpretation may be somewhat oversimplified; normal product distributions are found when pyridine and piperidine are used in the presence of peroxides, or with triethylamine in the absence of peroxides (Table III). On the other hand, under peroxide-free, light-free conditions pyridine effects little acceleration and the product contains considerably decreased yield of cyclohexenyl bromide and increased yield of addition dibromide (Table I). Thus, it would appear that triethylamine, but not pyridine, undergoes oxidation–reduction-displacement on NBS, although light may induce reaction of pyridine as it does in similar cases,[35] while both of these amines show the oxidation–reduction reaction with hydroperoxides.

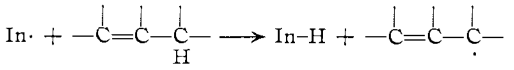
Mechanism.—In 1944, Bloomfield[8b] proposed that the allylic bromination of alkenes by NBS occurred by a radical chain mechanism involving initiation (thermally) by (1), propagation by (3) and (4), and termination by (5). The present results are in good agreement with the proposed propagation reactions but indicate that initiation and termination of the allylic bromination reaction, as usually conducted, occur by different reactions from those proposed by Bloomfield.

Initiation

$$\mathrm{(CH_2CO)_2N{-}Br} \longrightarrow \mathrm{(CH_2CO)_2N}\cdot + \cdot\mathrm{Br} \qquad (1)$$

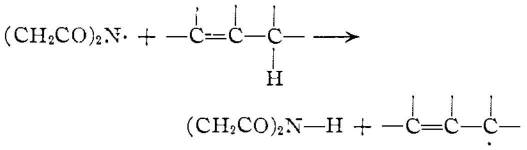
$$\mathrm{In{-}In} \longrightarrow 2\,\mathrm{In}\cdot \qquad (2a)$$

$$\mathrm{In}\cdot + \mathrm{(CH_2CO)_2N{-}Br} \longrightarrow \mathrm{In{-}Br} + \mathrm{(CH_2CO)_2N}\cdot \qquad (2b)$$

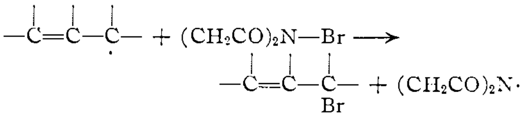


$$\mathrm{In}\cdot + -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}- \longrightarrow \mathrm{In{-}H} + -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\cdot}{\overset{|}{\mathrm{C}}}- \qquad (2c)$$

Propagation

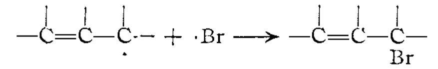


$$\mathrm{(CH_2CO)_2N}\cdot + -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}- \longrightarrow \mathrm{(CH_2CO)_2N{-}H} + -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\cdot}{\overset{|}{\mathrm{C}}}- \qquad (3)$$

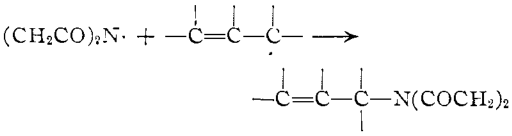


$$-\underset{\cdot}{\overset{|}{\mathrm{C}}}=\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}- + \mathrm{(CH_2CO)_2N{-}Br} \longrightarrow -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\mathrm{Br}}{\overset{|}{\mathrm{C}}}- + \mathrm{(CH_2CO)_2N}\cdot \qquad (4)$$

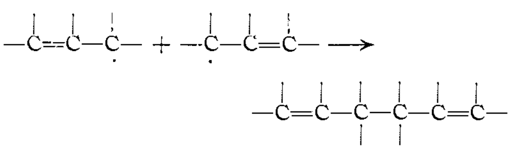
Termination



$$-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\cdot}{\overset{|}{\mathrm{C}}}- + \cdot\mathrm{Br} \longrightarrow -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\mathrm{Br}}{\overset{|}{\mathrm{C}}}- \qquad (5)$$



$$\mathrm{(CH_2CO)_2N}\cdot + -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\cdot}{\overset{|}{\mathrm{C}}}- \longrightarrow -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{N(COCH_2)_2} \qquad (6a)$$



$$-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{\cdot}{\overset{|}{\mathrm{C}}}- + -\underset{\cdot}{\overset{|}{\mathrm{C}}}-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}- \longrightarrow -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\underset{|}{\overset{|}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{C}}}-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}- \qquad (6b)$$

$$\mathrm{(CH_2CO)_2N}\cdot + \cdot\mathrm{N(COCH_2)_2} \longrightarrow \text{inactive products} \qquad (6c)$$

$$\mathrm{(CH_2CO)_2N}\cdot + \mathrm{T} \longrightarrow \text{inactive products} \qquad (6d)$$

Evidence now available, largely from the present work, indicates that the reaction is initiated by the following methods: (i) possibly by thermal homolysis of NBS at elevated temperatures[39] but not at the usual reaction temperature (80°); (ii) probably by thermal or photochemical homolysis of bromine, inadvertently introduced as an impurity in the NBS or formed by reaction of NBS with water or hydrogen bromide impurities, the latter also being formed by elimination from the allylic bromide product; (iii) by photolysis of NBS, even in diffuse daylight[40]; (iv) by thermal decomposition of well-known radical sources, alkyl hydroperoxides, diaroyl peroxides or azo-bis-nitriles, either deliberately added or in the case of allylic hydroperoxides, conveniently present as an autoxidation impurity in the alkene[41]; (v) by oxidation–reduction-decomposition of hydroperoxides with NBS or added *t*-amines, or of NBS with *t*-amines. In the simplest and most general form, chain-starting occurs by thermal dissociation of the initiators (2a) to produce radicals that react with NBS (2b) or with alkene (2c) to start the propaga-

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[36] The percentage yields reported by Braude and Waight[8c] for the monobromide fraction are too low and for the "1,2-dibromocyclohexane" fraction are too high because their refractometric method of analysis was based on the incorrect assumption that the only bromo products present were 3-bromocyclohexene ($n^{20}\mathrm{D}$ 1.5270) and 1,2-dibromocyclohexane ($n^{20}\mathrm{D}$ 1.5516). The present study has shown that the dibromide fraction contains 3,6-dibromocyclohexene ($n\mathrm{D}$ *ca.* 1.57) as the major component (10–13% yield) and 1,2-dibromocyclohexane as only a minor one (1–4% yield) (Table I). The yields reported by Bailey and Bello[8g] are subject to the same error.

[37] The allylic bromination reaction induced by 0.5 mole per cent. tetralyl hydroperoxide also is considerably accelerated (2–3 fold) by the addition of 0.75 mole per cent. pyridine.

[38] C. H. Tipper, *J. Chem. Soc.*, 1675 (1953), has found that pyridine greatly accelerates the decomposition of 9-decalyl hydroperoxide; his observation that trace impurities must be removed from the pyridine before its catalytic action is shown may explain the report of Stannett and Mesrobian[24a] that decomposition of *t*-butyl hydroperoxide is not appreciably accelerated by pyridine. H. Fikentscher and K. Herrle, B.I.O.S. Report 354, Item 22 (quoted in C. H. Bamford, W. G. Barb, A. D. Jenkins and P. F. Onyon, "The Kinetics of Vinyl Polymerization by Radical Mechanisms," Butterworth, 1958, p. 225) have shown that aliphatic amines induce the oxidation–reduction-decomposition of hydrogen peroxide.

[39] 1-Phenylpropene[5] and 1,2-diphenylpropene (A. Lüttringhaus, H. B. König and B. Böttcher, *Ann.*, **560**, 201 (1947)) give allylic bromide products only at elevated temperatures.

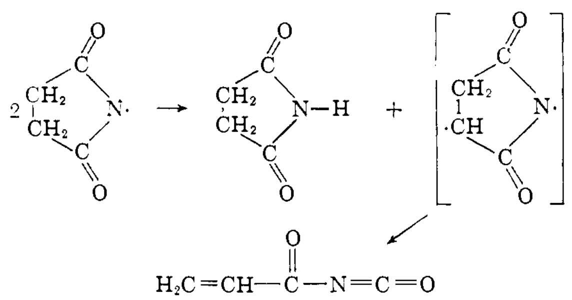
[40] Benzylic halogenations of toluenes by NBS or NCS are also light-catalyzed[7a,c] but only the former reaction appears to follow an analogous mechanism involving succinimidyl radicals as chain carriers[5e]; in the NCS reaction toluene seems to be tbe photosensitive reactant and chlorine radicals the chain-carriers.[7e]

[41] Toluene, which does not form a hydroperoxide on autoxidation (C. Walling and S. A. Buckler, THIS JOURNAL, **77**, 6032 (1955)), fails to undergo benzylic bromination by NBS unless other initiators or light are added.[8c]

tion steps.[42] Estimated heats of reaction of various initiator fragments with NBS or with cyclohexene indicate that both types of reaction will be about equally exothermic so that steps 2b and 2c are about equally probable.[42]

The propagation steps (3 and 4) would be expected to have the low heats of reaction (respectively, + 1 and − 3.5 kcal. mole^{-1})[42] necessary for an efficient chain reaction and both kinetics[42] and energy considerations indicate that (3), abstraction of allylic hydrogen by succinimidyl radical, should be slower than (4), abstraction of bromine from NBS by allylic radical. With (3) being rate-determining, succinimidyl radicals should be the chain-carrying radicals; the negative ρ-value for the reaction of NBS with substituted toluenes[7b] and our finding that electron-accepting chain terminators are only moderately effective retarders support this contention that electron-accepting succinimidyl radicals, rather than electron-donating allylic radicals, are the chain carriers. The high electron affinity of succinimidyl radicals and the low ionization potentials of allylic radicals undoubtedly reduce activation energies for (3) and (4) by introducing polar structures in their transition states.[43]

Inasmuch as bromine radicals are not usually involved in the NBS-allylic bromination reaction, the proposal by Bloomfield[8b] that chain termination occurs by the coupling of allyl and bromine radicals (5) becomes untenable. Chain termination would be expected to result from the reaction of propagation radicals, allyl or succinimidyl, with each other (6a) or with another of the same type (6b or 6a) to produce relatively stable product(s). Estimated bond dissociation energies indicate that stable products should be formed by (6a) or (6b) but that (6c),[42] the coupling of two succinimidyl radicals to give bis-N-succinimidyl (estimated $D((CH_2CO)_2N\text{-}N\text{-}(COCH_2)_2)$ = 0 kcal. mole^{-1}), should not be possible due to the high resonance stabilization of succinimidyl radicals (estimated RE = 30 kcal. mole^{-1}). For this reason it is not surprising that attempts to prepare bis-N-succinimidyl have been unsuccessful.[8f] Kinetic studies[42] indicate, however, that chain termination most likely takes place by some type of reaction between two succinimidyl radicals to give stable products. A plausible reaction might involve the abstraction of an α-hydrogen from one succinimidyl radical by another to give succinimide and a diradical intermediate that stabilizes itself intramolecularly by ring cleavage to form acryl isocyanate; under certain reaction conditions the latter product may be converted subsequently into β-bromo- or α,β-dibromopropionyl isocyanate.[44]



In view of the long chain length of the allylic bromination reaction[42] it should not be possible, except by isotopic dilution techniques, to identify the chain termination reaction and products. For reasons advanced earlier, added inhibitors probably terminate the reaction by reacting with the chain carrying succinimidyl radicals (6d).

Experimental

All boiling points and melting points are uncorrected.

General Procedure.—In all runs the reactants were used in the proportions of 1 mole NBS/1.5 moles cyclohexene/750 moles carbon tetrachloride/*ca.* 0.01 mole modifier, when added,[45] which corresponds to stoichiometrical concentrations of 1.11 moles of NBS (solubility in carbon tetrachloride, *ca.* 0.006 mole/liter at 50°),[12a] 1.66 moles of cyclohexene, and *ca.* 0.011 mole of modifier per liter of carbon tetrachloride. With the exception of a few runs in the study of environmental factors, NBS, carbon tetrachloride, cyclohexene and modifier were added to the reaction flask in that order and then brought to reflux on a steam-cone as rapidly as possible; the period of heating from room temperature to reflux was about 10–15 seconds for small scale runs and 2–4 minutes for large scale runs. Unless otherwise noted, small scale runs for comparison of reaction times used 0.0067 mole of NBS, while large scale runs for product analysis employed 0.10 mole of NBS. The time for complete reaction is reported as a range; the lower limit indicates the last time at which a positive test for positive bromine was obtained with moistened starch–iodide paper and the upper limit the time for the first negative test, tests being made externally on small samples removed from the reaction mixture. Visual observation of whether or not all of the subnatant NBS had been converted to supernatant succinimide served as a check on the starch–iodide test. C.P. grade carbon tetrachloride (Coleman and Bell, Baker analyzed) was used in all runs reported without purification. Runs using C.P. grade carbon tetrachloride from different bottles gave satisfactory, reproducible results, but technical grades gave erratic results. In the following sections, only the number of moles of NBS and the conditions other than those already specified will be given when describing the various runs.

Purification of NBS.—Commercial samples (Arapahoe Chemical Co.; National Aniline Div., Allied Chemical and Dye Corp.) initially available were of variable quality, ranging in color from white to deep yellow, presumably due to occluded bromine. Rapid recrystallization from boiling water[5] or from acetic acid[46] have been recommended for purification of NBS, but benzene is not satisfactory.[5] To ascertain whether recrystallization from water would give satisfactory material for comparative studies, purification was carried out by four slightly different techniques. A. NBS (30 g.) was added to boiling water (300 ml.), swirled for about one minute to complete dissolution, filtered rapidly through a fluted filter into a flask immersed in an ice-bath,

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[42] Mechanistic conclusions in this paper are in accord with those established by collateral kinetic studies (H. J. Dauben, Jr., and E. A. Youngman, ref. 12a); reaction of NBS with cyclohexene in degassed benzene solutions at 20–40° with azo-bis-isobutyronitrile initiator had a chain length of about 2800 and followed the rate expression, $-d[NBS]/dt = k[\text{cyclohexene}][\text{initiator}]^{1/2}$, which corresponded to steps 2a, 2b or 2c, 3 and 4 with 3 being slower, and 6c although 6a or 6b would be possible under certain conditions. Energy considerations using $D((CH_2CO)_2N\text{-}H)$ = 74, $D((CH_2CO)_2N\text{-}Br)$ = 44, D(cyclohexenyl–H) = 75, D(cyclohexenyl–Br) = 47.5 kcal. mole^{-1} predict heats of reaction for steps 3 and 4 of +1 and −3.5 kcal. mole^{-1}, respectively.

[43] The same suggestion has been made recently by Green, Remers and Wilson[7d] and by G. A. Russell (*J. Org. Chem.*, **23**, 1407 (1958)).

[44] A somewhat similar mechanism has been proposed recently by Martin and Bartlett[8h] to explain the formation of β-bromopropionyl isocyanate when NBS is refluxed in carbon tetrachloride with strong irradiation or with benzoyl peroxide; the same product has been obtained under slightly different conditions (H. W. Johnson, Jr., and D. E. Bublitz, THIS JOURNAL, **79**, 753 (1957), and **80**, 3150 (1958)).

[45] The actual mole per cent. of modifier varied from 0.87 to 1.92, being about 1.0 in most runs, but sufficient runs were made with each substance to show that in this range the effect of each modifier was essentially constant.

[46] E. Campaigne and B. F. Tullar, *Org. Syntheses*, **33**, 97 (1953).

and allowed to stand in the ice-bath for 2 hours. The NBS crystals were filtered, washed thoroughly with ice-cold water (*ca.* 100 ml.) and drained on the Büchner funnel. This material was divided into two parts for drying by different methods: (a) standing in open air for 3 days; (b) drying in a pistol over phosphorus pentoxide at 77° (15 mm.) for 12 hours and then at room temperature for an additional 2 days. B. The same procedure as in method A was used except that the hot filtrate was allowed to cool slowly at room temperature; portions of B then were dried by methods a and b. The four different samples were analyzed iodometrically for active bromine and the times for complete reaction determined using cyclohexene freshly distilled from sodium. The results obtained indicate that the reactivity is independent of the recrystallization technique but is dependent on the drying procedure used.

Method of purif.	Recovery, %	Act. Br, %	Time for complete run., min.
Aa	83	99.4	100–104
Ab		99.5	165–171
Ba	67	99.0	108–112
Bb		99.6	158–162

After it had been shown that different samples of NBS purified by method Aa gave consistent reaction times and sufficiently consistent relative reactivity values,[47] NBS purified by method Aa was used in all of the following runs.

Effect of Peroxides in Cyclohexene.—Cyclohexene (Eastman white label grade) was refluxed over sodium for about 30 min. and then distilled from fresh sodium; the portion having b.p. 82.0–82.5° was stored in a glass-stoppered bottle. At intervals of 3 days samples were removed and analyzed for peroxides.[48] At the time of each analysis a 0.0067-mole run was made, the same lot of NBS being used throughout the complete series of runs. A second series, using different lots of cyclohexene and NBS and analyzed for peroxides and reaction times at more random time intervals, gave similar results. Results for both series are summarized in Fig. 1.

Three samples of aged cyclohexene (52–53 day-old cyclohexene of series 2, 0.176–0.184 M in peroxides) were diluted with cyclohexene freshly distilled from sodium. The samples prepared in this way had peroxide concentrations[48] of 0.0092, 0.0176 and 0.0276 M and were found to give reaction times of 108–111, 83–86 and 59–62 min., respectively. After converting the peroxide concentrations to their equivalent number of days of aging, the three results were plotted and compared with the reaction time curve (Fig. 1, series 2).

Large Scale Control Run.—The following 0.10-mole run was used as a standard for comparison with other large scale runs; the cyclohexene was 0.022 M in peroxides and the time for complete reaction was 70–75 min. The reaction mixture was cooled in an ice-bath, suction filtered, and the succinimide washed with carbon tetrachloride (15 ml.); yield of succinimide, 9.8 g. (99%), m.p. 125–126°. (In all runs analyzed for products, yields of 98–101% succinimide were obtained unless otherwise specified.) The filtrate and washings were combined, carbon tetrachloride was removed under reduced pressure (water aspirator), and the residue distilled through a modified Claisen head with 4-in. Vigreux column to give the fractions

Fraction	1	2	3	Residue	Total[a] yd., %
B.p. (11 mm.), °C.	55–57[b]	57–100	100–105		
n^{20}D	1.5308[b]				
Wt., g.	9.95	0.99	1.35	1.34	
3-Bromocyclohexene, %	61.9	2.4			64.3
3,6-Dibromocyclohexene, %		5.0	10.2		15.2
1,2-Dibromocyclohexane, %			1.0		1.0
Bromine (% organically bound Br)				7.0	7.0
3-Bromocyclohexene lost by codistillation with CCl_4, %					*ca.* 10.0
					97.5

[a] Yields based on NBS. [b] Reported b.p. and nD: 58–60° (12 mm.), 1.5309 (18.5°), E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951); 1.5270 (20°), ref. 8f; 77–83° (35 mm.), 1.5279 (20°), J. D. Park, W. R. Lycan and J. R. Lacher, THIS JOURNAL, **76**, 1388 (1954).

To correct for the 3-bromocyclohexene lost by codistillation with carbon tetrachloride, pure 3-bromocyclohexene (10.0 g.) was mixed with carbon tetrachloride (75 ml.) and the mixture was worked up in the same way as in the control run; recovery was 8.60 g. (86%) of 3-bromocyclohexene with a residue of less than 0.1 g. Fractions 2 and 3 were analyzed for double bonds,[49a] and for bromine by a modified Stepanow method.[49b] Using these data and the weights of fractions 2 and 3 and assuming that only 3-bromocyclohexene, 3,6-dibromocyclohexene and 1,2-dibromocyclohexane are present, the amount of each component present in these fractions may be estimated. 3,6-Dibromocyclohexene, m.p. 110–111° after recrystallization from petroleum ether (30–60°), could also be isolated from fraction 3 by a method similar to that of Howton.[50]

Effect of Environmental Factors.—These runs were 0.10-mole size except run 6 (Table II) which was 0.04 mole. In runs without a nitrogen atmosphere the cyclohexene was 0.022 M in peroxides, prepared by diluting aged cyclohexene containing a known peroxide concentration with peroxide-free cyclohexene. In runs using a nitrogen atmosphere the cyclohexene was distilled from sodium in a nitrogen atomosphere directly into the reaction flask which previously had been swept out with nitrogen. The reaction flask was a three-necked, cone-shaped, 125-ml. flask equipped with a reflux condenser and a gas inlet tube that could be lowered or raised to allow nitrogen to pass through the reaction mixture or over its surface. In all runs with nitrogen, it was passed through an electrically-heated column filled with copper turnings to remove traces of oxygen. After adding the carbon tetrachloride and NBS, the apparatus was flushed by bubbling deoxygenated nitrogen through the reaction mixture for 15 minutes before heating to reflux. During the reaction the nitrogen inlet was raised above the surface of the reaction mixture. Runs in the dark were made in a flask covered with black lacquer or a black cloth and the apparatus was set up in a dark hood. Samples were removed at intervals by increasing the nitrogen flow through the system, then quickly unstoppering the third neck of the flask, removing the sample, restoppering, and finally reducing the flow of nitrogen. After determining the time of complete reaction, the mixture was worked up as in the control run. Since fraction 2 contained both mono- and dibromides, only fractions 1 and 3 were used in comparing yields; by assuming that fraction 3 consisted only of 3,6-dibromocyclohexene and 1,2-dibromocyclohexane the relative amounts of these two dibromides could be determined by analysis for double bonds.[49a] The results of these are summarized in Table I.

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[47] Complete reaction times for different lots of NBS purified by method Aa in unmodified runs usually were about 110 ± 10 min., but in a few extreme cases were as high as about 140 min. and as low as about 60 min. Reaction times in modified runs showed much less variation (usually about ±5 min.) and relative reactivities on different lots were reasonably consistent. Subsequent kinetic studies[12a] have shown that in peroxide-catalyzed runs samples of NBS recrystallized from water and then dried either over calcium chloride or phosphorus pentoxide, or by sublimation, all react at the same rate. These observations indicate that air-dried samples of NBS probably contain variable trace amounts of catalytic impurities (water, hydrogen bromide or bromine) that are removed only by drying under reduced pressure or by sublimation; their effect is overwhelmed when catalysts or inhibitors are deliberately added.

[48] C. C. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 977 (1947).

[49] (a) S. Siggia, "Quantitative Organic Analysis via Functional Groups," 1st Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 33; (b) R. L. Shriner, "Quantitative Analysis of Organic Compounds," Edwards Brothers, Ann Arbor, Mich., 1946, p. 71.

[50] D. R. Howton, THIS JOURNAL, **69**, 2060 (1947), reported m.p. 107.5–108.3°; Ziegler, *et al.*,[5] found m.p. 108°. In similar runs, it was also possible, after removing 3-bromocyclohexene by distillation, to extract 3,6-dibromocyclohexene from the pot residue by petroleum ether (30–60°).

Thermal Decomposition of 3-Bromocyclohexene.—Pure 3-bromocyclohexene (10.0 g., 0.062 mole) was mixed with carbon tetrachloride (75 ml.) and refluxed for 2 days. During this period a very slow stream of nitrogen swept out any gaseous products into a Dry Ice trap and then into an aqueous 5% silver nitrate solution. The silver nitrate solution developed only a very faint cloudiness. The carbon tetrachloride solution was diluted to 100 ml. and two 5-ml. aliquots were analyzed for double bonds[49a]; found: 0.0682, 0.0685 total equivalent of double bonds. This represents about a 10% increase in the number of double bonds over that present in the starting material. The remainder of the mixture was worked up as in the control run and gave 3-bromocyclohexene (7.4 g., b.p. 59–60° (15 mm.), $n^{20}{}_{D}$ 1.5304) and a dark residue (0.9 g.). The small amount of material in the Dry Ice trap apparently was largely hydrogen bromide; it fumed strongly in air and with gaseous ammonia, the fumes being acid to litmus, and gave instantaneously a light yellow precipitate with aqueous silver nitrate. Pure 3-bromocyclohexene does not fume in air or with gaseous ammonia and its reaction with aqueous silver nitrate, although rapid, is not instantaneous.

Effect of Modifiers on Reaction Time.—At least two runs (0.0067-mole size) were made with each substance studied, with an average of a little more than three runs per substance. In these runs the time for complete reaction was taken as the value midpoint of the range usually given; the difference between the upper and lower limits of this range was 6 min. for the long runs (>90 min.) and decreases to 2 min. for short runs (<15 min.). All of the modifiers were tried on cyclohexene 0.022 *M* in peroxide, prepared by diluting cyclohexene freshly distilled from sodium with aged cyclohexene containing less than 0.150 *M* peroxide. About one-third of the modifiers were also tried with cyclohexene freshly distilled from sodium (essentially peroxide-free cyclohexene) and with cyclohexene 0.088 *M* in peroxide. In the runs using cyclohexene containing 0.022 or 0.088 *M* peroxide, the resultant concentrations of cyclohexenyl hydroperoxide in the reactant solutions were, respectively, 0.0037 or 0.0148 *M*; on the same basis, limiting reaction times in Fig. 1 were found to occur at peroxide concentrations of about 0.006 *M*. The results of these runs are summarized in Table II as relative reactivities, *i.e.*, the ratio of the time of reaction for an unmodified run to the time of reaction for a modified run, both runs being made with the same reagents. This means of comparing results was necessary since it was observed that different batches gave somewhat different reaction times even though purified in an apparently identical manner; expressed in this manner the relative reactivities were fairly reproducible and independent of the batch of NBS used. Relative reactivities were difficult to reproduce when hydroquinone or tetrabromohydroquinone were used, probably due to their marked insolubility in carbon tetrachloride, and when water was added as modifier; a small amount of water very finely dispersed in the carbon tetrachloride usually gave a strong catalytic effect while an equal quantity of water present as two or three relatively large droplets showed essentially no effect. The actual times for runs summarized in Table II varied from 14 min. to greater than 688 min. for 0.00 *M* peroxide runs, from 8 min. to greater than 240 min. for 0.022 *M* peroxide runs, and from 5 min. to greater than 71 min. for 0.088 *M* peroxide runs.

Several check runs were made using modifiers with a nitrogen atmosphere but no differences in reaction times were observed. However, some evidence has been obtained which indicates that dissolved oxygen may act as an inhibitor. Cyclohexene, artificially aged by bubbling oxygen through it at room temperature for several minutes and then allowing it to stand in a stoppered bottle for 2–3 days, was 0.0353 *M* in peroxide and gave a reaction time of 80–85 min. After deoxygenation by bubbling oxygen-free nitrogen through it for 1 hr., the cyclohexene then was 0.0303 *M* in peroxide and showed a reaction time of 70–75 min. Providing that the presence of dissolved oxygen does not interfere with the accuracy of the determination of peroxide concentrations, as found by another analytical method,[23d] the shorter reaction time given by the deoxygenated cyclohexene possibly indicates an inhibitory effect of oxygen.

Effect of Modifiers on Yields of Products.—These 0.10-mole runs were made with cyclohexene 0.022 *M* in peroxide, except for the use of peroxide-free cyclohexene in the triethylamine run; the amounts of modifiers used, in mole per cent., were: 1% azo-bis-isobutyronitrile, 1% benzoyl peroxide, *ca.* 2–3% hydrogen bromide, 2% piperidine, 2% pyridine, 2% triethylamine and *ca.* 1–3% water. The runs were conducted in the same way as for the control run and again only distillation fractions 1 and 3 were used for comparing yields with the control run. The results are summarized in Table III.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY RUTGERS, THE STATE UNIVERSITY]

The Effect of Structure on the Course of Phosphoryl Chloride–Pyridine Dehydration of Tertiary Alcohols

BY RONALD R. SAUERS

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The scope of phosphoryl chloride–pyridine dehydration of tertiary alcohols has been broadened by a study of several types of model compounds. Steric effects play a large role in controlling the direction of elimination.

Recent interest in the direction of elimination of various groups from tertiary centers[1] as well as the desire to extend the scope of phosphoryl chloride–pyridine dehydration of alcohols prompted a study of the dehydration of several model tertiary alcohols. Examples were taken from the following categories: aliphatic, alicyclic and bicyclic.

Results and Discussion

Aliphatic.—Dehydration of 2-methyl-2-butanol with phosphoryl chloride in the presence of a large excess of pyridine gave a mixture of 2-methyl-2-butene (73%) and 2-methyl-1-butene (27%). Since it was shown that the ratio of products was not affected by the reaction conditions, the fact that the yields are sometimes low is probably of little significance.

The product composition found is not surprising in view of the experiments of Brown and Moritani[1c] who demonstrated the importance of the steric requirements of the leaving group in elimination reactions. A close analogy to the present work involved the dehydration of 2-methyl-2-butanol with *p*-toluenesulfonyl chloride and pyridine.[2] The mixture of olefins obtained (63:37) agrees qualitatively with the present results.

Alicyclic.—1-Methylcyclopentanol, 1-methylcyclohexanol and 1-methylcycloheptanol were pre-

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(1) (a) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, THIS JOURNAL, **79**, 4729 (1957); (b) H. E. Baumgarten, F. A. Bower, R. A. Setterquist and R. E. Allen, *ibid.*, **80**, 4588 (1958); (c) H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956); (d) R. A. Benkeser and J. Hazdra, *ibid.*, **81**, 228 (1959).

(2) Although the exact nature of the leaving group has not been determined in either case, it seems reasonable to assume that ester formation[1c] ($R-OSO_2C_7H_7$ and $R-OP(O)Cl_2$) precedes elimination.