gave unreacted octene-1 (3.5 g.), cyclohexanol, 1-*n*-octylcyclohexanol (1.8 g., b.p. 105–115° at 1 mm., $n^{25}\mathrm{D}$ 1.4628) and a residue (3 g.).

Attempted Additions with Other Free Radical Initiators.—A number of possible free radical initiators gave negative results in test systems containing cyclohexanol (250 g., 2.50 moles) and octene-1 (11.2 g., 0.10 mole): (1) α-cumyl hydroperoxide (4.5 g.) at 150° for 48 hours; (2) hexachloroethane (2.4 g.) at 150° for 48 hours; and (3) a solution of benzoyl peroxide (2.4 g.) in chlorobenzene (20 ml.) added over 8 hours at 140° (12 hours at 140° after addition). In all cases the cyclohexanol and octene-1 were recovered quantitatively, and no residues were obtained.

A solution of benzoyl peroxide (2 g.) and octene-1 (26.5 g., 0.22 mole) in propanol-2 heated under reflux (80–81°) for 24 hours gave no addition product. Acetone (0.45 g.) was obtained. Propanol-2 and octene-1 in the same amount with 2,2′-azo-bis-isobutyronitrile (1.6 g.) at 80° for 20 hours gave no addition reaction. A small residue (0.5 g.) obtained after distillation contained tetramethylsuccinonitrile (m.p. 166–168° after recrystallization from ethanol, 80%).[20] A small amount of acetone (0.1 g.) was also found.

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[20] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

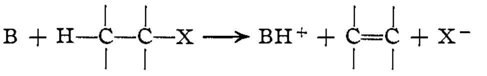
Rate Data for the Bimolecular Elimination Reactions of the *t*-Amyl Halides. Further Evidence for the Concerted Nature of Bimolecular Eliminations

BY HERBERT C. BROWN AND ICHIRO MORITANI[1]

RECEIVED JUNE 12, 1953

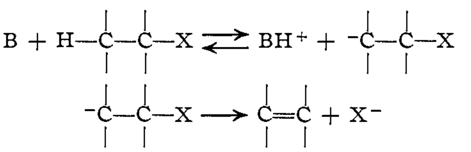
The first-order reactions of *t*-amyl bromide with methyl, ethyl, isopropyl and *t*-butyl alcohols have been investigated and compared with the second-order reactions with the corresponding potassium alkoxides in the same solvents. The reaction with potassium *t*-butoxide in *t*-butyl alcohol is considerably faster than the first-order reaction in that solvent. This reaction therefore furnishes a convenient procedure for investigating bimolecular eliminations involving tertiary halides. The rate constants ($k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$) vary markedly with the halogen: *t*-amyl chloride, 0.00583; bromide, 0.338; iodide, 2.34. These results can best be explained by the simultaneous loss of hydrogen and halogen and are therefore consistent with the concerted mechanism for bimolecular elimination in tertiary halides.

Considerable interest has been expressed in whether bimolecular eliminations involve one- (I) or two-stage (II) processes.[2]



$$\mathrm{B + H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \longrightarrow BH^+ + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} + X^-} \qquad \text{(I)}$$

or



$$\mathrm{B + H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \rightleftarrows BH^+ + {}^-\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} \qquad \text{(II)}$$

$$\mathrm{{}^-\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \longrightarrow \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} + X^-}$$

Skell and Hauser[3] and Shiner[4] utilized deuterium in a study of this question in the elimination reactions of β-phenylethyl and isopropyl bromides. They concluded that the elimination process is concerted. In the course of an extended study of bimolecular eliminations in benzene hexachloride and various *cis–trans* isomeric compounds, Cristol and his co-workers have concluded that a concerted mechanism is involved when the hydrogen and halogen undergoing elimination are *trans* and can assume a planar transition state.[5]

Barton and his co-workers have reached the same conclusions as a result of his investigations of conformational effects in steroid systems.[6] Finally, Doering and Meislich observed that in optically active trimethyl-β-phenylisopropylammonium ion racemization did not accompany elimination and concluded that a concerted process was also involved in bimolecular eliminations in these compounds.[7]

These studies have largely dealt with eliminations from primary and secondary alkyl groups: $C_6H_5CH_2CH_2Br$,[3] $CD_3CHBrCD_3$,[4] $C_6H_6Cl_6$[5] and $C_6H_5CH_2CH(N^+Me_3)CH_3$.[7] In the course of a study we have been making of the effect of steric strains in directing the course of elimination reactions, we had developed an improved procedure for following the rates of bimolecular elimination reactions of tertiary halides. It appeared that a kinetic study of the rates of elimination of selected tertiary halides might provide an answer to the question whether the one-stage process is also involved in bimolecular elimination of such compounds. Accordingly, a kinetic study was undertaken of bimolecular elimination in *t*-amyl chloride, bromide and iodide.

Results and Discussion

In the case of secondary alkyl halides, the rates of bimolecular elimination are usually followed by observing the reaction of the halide with ethoxide ion in absolute ethanol.[4,8] This procedure offers difficulties in the case of tertiary halides. With these compounds the solvolysis reaction is so fast that the bimolecular elimination reaction with the base becomes the predominant reaction only at very high concentrations of the base. With increasing steric requirement of the alkyl groups attached to the central atom, R_3CX, the rate of the solvolytic reaction increases[9] and that of the bimolec-

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[1] O. N. R. Post-doctorate Fellow at Purdue University, 1951–1953.

[2] For a recent review of the mechanism of elimination reactions and detailed references to the literature, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. VIII.

[3] P. S. Skell and C. R. Hauser, THIS JOURNAL, **67**, 1661 (1945).

[4] V. J. Shiner, Jr., *ibid.*, **74**, 5285 (1952).

[5] S. J. Cristol, *ibid.*, **69**, 338 (1947); S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952), S. J. Cristol and A. Begoon, *ibid.*, **74**, 5025 (1952).

[6] D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950); D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

[7] W. von E. Doering and H. Meislich, THIS JOURNAL, **74**, 2099 (1952).

[8] M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948).

[9] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

ular elimination reaction decreases.[10] With these compounds it becomes very difficult to observe the kinetics of the bimolecular elimination reaction.

A study was made of the relative magnitudes of the first-order (solvolysis) and the second-order (t-AmBr + RO^-K^+) reactions of *t*-amyl bromide in methyl, ethyl, isopropyl and *t*-butyl alcohols. The results are summarized in Table I.

TABLE I

RATE DATA FOR THE FIRST- AND SECOND-ORDER REACTIONS OF *t*-AMYL BROMIDE AT 25°

	First-order reaction			Second-order reaction[a]	
Alcohol	$k_1 \times 10^5$ (sec.$^{-1}$)	Reacted in 3 hours, %	Base	$k_2 \times 10^5$ (l. mole^{-1} sec.$^{-1}$)[b]	Reacted in 3 hours, %
Methyl	7.3	54.8	$CH_3O^-K^+$	(3.29)[c]	61.8
Ethyl[d]	0.96	7.5	$C_2H_5O^-K^+$	1.51	40.5
Isopropyl	.26	2.8	$(CH_3)_2CHO^-K^+$	0.769	25.8
t-Butyl	.090	1.1	$(CH_3)_3CO^-K^+$	0.338	14.8

[a] Concentration of base and alkyl halide equal, approximately 1 *M*. [b] Calculated from amount of base reacted ignoring concurrent solvolysis of alkyl halide. [c] See footnote *c* in Table IV. [d] In presence of 1 *M* potassium iodide $k_1 \times 10^5$ increased from 0.96 to 1.3 (sec.$^{-1}$).

In the case of the *t*-butyl alcohol–*t*-butoxide system, the relative rates of the first- and second-order reactions are particularly favorable to permit following the second-order elimination reaction. In the presence of 1.0 *M* potassium *t*-butoxide it was estimated that approximately 93% of the *t*-amyl bromide reacting was undergoing bimolecular elimination with the base, with only 7% reacting by a concurrent solvolytic reaction. The system possesses the further advantage with both secondary and tertiary halides of giving very little substitution. Yields of olefins as high as 90–96% were readily isolated from the reaction mixtures. This reaction was therefore adopted for our studies of the effect of structure on the rate of bimolecular eliminations of alkyl halides.

The results obtained with the *t*-amyl halides are summarized in Table II.

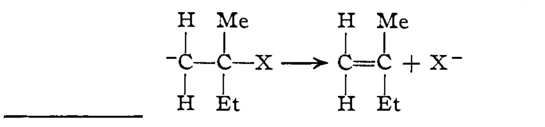
TABLE II

RATE CONSTANTS FOR THE SECOND-ORDER REACTION OF THE *t*-AMYL HALIDES WITH *t*-BUTOXIDE IN *t*-BUTYL ALCOHOL AT 25°

t-Amyl halide	Rate constant[a] $k_2 \times 10^5$ (l. mole^{-1} sec.$^{-1}$)
Chloride	0.00583
Bromide	0.338
Iodide	2.34

[a] The small amount of concurrent solvolytic reaction was ignored in calculating the second-order rate constant.

If a two-stage process were involved in this reaction with the first step rate-determining



$$t\text{-BuO}^- + \text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{Me}}{\underset{\text{Et}}{\text{C}}}-\text{X} \rightleftharpoons t\text{-BuOH} + {}^-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{Me}}{\underset{\text{Et}}{\text{C}}}-\text{X}$$

$$ {}^-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{Me}}{\underset{\text{Et}}{\text{C}}}-\text{X} \longrightarrow \overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{Me}}{\underset{\text{Et}}{\text{C}}} + \text{X}^-$$

we should expect that the reaction rate should be largely independent of the halogen, X. If the halogen exerted any significant influence on the first step, the greater electronegativity of chlorine should favor the removal of the proton and the rate should then decrease with the decreasing electronegativity of the halogen: RCl > RBr > RI. However, the opposite is observed. If a two-stage process is involved, it follows that the second stage must be rate determining. This does not appear likely in these compounds. It follows that the results can best be explained by the simultaneous loss of hydrogen and halogen.

It should be pointed out that Ingold and his co-workers had previously observed that the reactivities of the isopropyl halides in elimination reactions vary in the order: chloride < bromide < iodide. Also Cram and Abd Elhafez[11] observed this order of reactivity in the assumed bimolecular eliminations of the 1,2-diphenyl-1-propyl halides. It therefore appears that observations of the effect of the halogen on rate of bimolecular eliminations may offer a useful general test for the existence of the concerted mechanism in a variety of systems.

Experimental Part

Materials.—The methyl, ethyl, isopropyl and *t*-butyl alcohols were the purest grades available. They were dried and distilled over calcium hydride. The *t*-amyl chloride, bromide and iodide were prepared from treatment of the alcohol with hydrogen chloride, bromide and iodide. The products were dried with magnesium sulfate and calcium hydride and distilled. The following physical constants were obtained:

	B.p., °C.	Mm.	$n^{20}D$
Methyl alcohol	64.2	746	1.3287
Ethyl alcohol	78.0	748	1.3622
Isopropyl alcohol	82.0	750	1.3776
t-Butyl alcohol	83.0	745	1.3877
t-Amyl chloride	84.3–85.0	741	1.4036
t-Amyl bromide	40.8–41.5	73	1.4412
t-Amyl iodide	33.0–33.5	19	1.4949

The First-Order Reaction.—*t*-Amyl bromide was dissolved in the four alcohols to make up a 1 *M* solution. (Solutions

TABLE III

RATE DATA FOR THE FIRST-ORDER REACTION OF *t*-AMYL BROMIDE IN SEVERAL ALCOHOLS

Methyl alcohol						
Time, hr.	∞	1.0	2.0	3.0	4.0	5.0
NaOH, ml.	4.275	0.930	1.700	2.345	2.910	3.200
$k_1 \times 10^5$, sec.$^{-1}$		6.7	6.9	7.5	7.8	7.5
Ethyl alcohol						
Time, hr.	∞	1.0	2.0	4.0	5.0	10.0
NaOH, ml.	4.140	0.145	0.260	0.365	0.687	1.300
$k_1 \times 10^5$, sec.$^{-1}$		0.92	0.94	0.94	1.0	1.0
Isopropyl alcohol						
Time, hr.	∞	1.0	2.0	3.0	5.0	7.0
NaOH, ml.	4.302	0.040	0.080	0.120	0.180	0.278
$k_1 \times 10^5$, sec.$^{-1}$		0.25	0.26	0.25	0.26	0.26
t-Butyl alcohol						
Time, hr.	∞	2.0	3.0	5.0	7.0	
NaOH, ml.	4.325	0.035	0.050	0.060	0.080	
$k_1 \times 10^5$, sec.$^{-1}$		0.10	0.10	0.077	0.083	
Ethyl alcohol (1.0 *M* potassium iodide)						
Time, hr.	∞	1.0	2.0	4.0	5.0	10.0
NaOH, ml.	4.210	0.200	0.385	0.740	0.910	1.660
$k_1 \times 10^5$, sec.$^{-1}$		1.3	1.3	1.3	1.4	1.4

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(10) Work in progress.

(11) D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **74**, 5851 (1952).

TABLE IV

RATE DATA FOR THE SECOND-ORDER REACTION OF *t*-AMYL HALIDES WITH POTASSIUM ALKOXIDE IN SEVERAL ALCOHOLS

Methyl alcohol, *t*-amyl bromide[a]						
Time, hr.	0	1.0	1.33	2.0	2.33	3.0
HCl, ml.[b]	4.423	2.897	2.592	2.170	1.999	1.690
$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$[c]		3.30	3.30	3.25	3.25	3.36
Ethyl alcohol, *t*-amyl bromide[a]						
Time, hr.	0	1.0	1.67	2.67	3.0	4.0
HCl, ml.[b]	4.133	3.375	3.003	2.582	2.460	2.091
$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$		1.51	1.52	1.51	1.52	1.51
Isopropyl alcohol, *t*-amyl bromide[a]						
Time, hr.	0	3.0	4.5	5.0	6.0	7.0
HCl, ml.[b]	4.232	3.138	2.772	2.660	2.476	2.308
$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$		0.761	0.767	0.775	0.775	0.769
t-Butyl alcohol, *t*-amyl bromide[a]						
Time, hr.	0	1.0	2.0	3.0	5.0	7.0
HCl, ml.[b]	3.860	3.682	3.532	3.375	3.133	2.912
$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$		0.347	0.333	0.344	0.333	0.333
t-Butyl alcohol, *t*-amyl chloride[a]						
Time, hr.	0	24.0	36.0	72.0	85.0	97.0
HCl, ml.[b]	4.537	4.427	4.343	4.235	4.189	4.145
$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$		0.00577	0.00591	0.00586	0.00583	0.00577
t-Butyl alcohol, *t*-amyl iodide[a]						
Time, hr.	0	0.33	0.67	1.0	1.33	1.5
HCl, ml.[b]	4.438	3.947	3.549	3.231	2.962	2.844
$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$		2.34	2.35	2.34	2.34	2.34

[a] Concentrations of *t*-amyl bromide and alkoxides were equal, approximately 1 *M*. [b] 1.145 *N*. [c] Since the quantity of halide which reacts in the presence of base is only slightly greater than the reaction observed in methanol alone, the calculation of k_2 must be meaningless. However, it is of interest that the calculation results in an excellent constancy in the value for k_2. We have not attempted to explore the reason for this constancy.

of this high concentration were utilized so that the rate data could be directly compared with those obtained for the second-order reaction.) Each reaction mixture of 100 ml. was maintained at 25.0°, 5.0-ml. aliquots removed at convenient time intervals, the reaction halted with cold (0°) absolute ethanol, and the acid formed titrated with 1.032 *N* sodium hydroxide. Typical rate data are summarized in Table III.

Second-Order Reaction.—Sufficient potassium was dissolved in the anhydrous alcohol and *t*-amyl bromide then added to make the solution approximately 1.0 *M* in both the alkoxide and halide. The reaction mixture was maintained at 25.0°. At suitable intervals 5.0-ml. aliquots were removed, added to cold (0°) absolute ethanol to halt the reaction, and the extent of reaction followed by titration for residual base. Typical rate data are summarized in Table IV.

Acknowledgment.—This investigation was carried out as part of a program supported by the Office of Naval Research at Purdue University on "Steric Strains in Chemical Reactions." This assistance is gratefuly acknowledged.

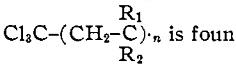
LAFAYETTE, INDIANA

[CONTRIBUTION NO. 130 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Additions of Chloroform and Carbon Tetrachloride to Allylic Monomers[1]

BY FREDERICK M. LEWIS[2a] AND FRANK R. MAYO[2b]

RECEIVED JULY 20, 1953

The benzoyl peroxide-initiated reactions of propylene, isobutylene, allyl acetate and allyl chloride with carbon tetrachloride, and of propylene and isobutylene with chloroform have been studied at 100°. Various monomer-solvent ratios and concentrations of initiator were employed in order to determine how the most addition product per initiator molecule can be obtained, and to distinguish among five possible mechanisms of chain termination. At 0.01 mole % of benzoyl peroxide, 600 moles of addition product could be obtained per mole of peroxide from isobutylene and carbon tetrachloride, only 3 moles from isobutylene and chloroform. Optimum solvent–monomer feed ratios varied from 1 to 10. Nearly all reaction mixtures gave products averaging more than one monomer unit per molecule. From the compositions of these products, the relative reactivity of solvent and monomer toward the radicals  $Cl_3C\text{–}(CH_2\text{–}\overset{R_1}{\underset{R_2}{C}})\cdot_n$ is found to increase at least fivefold as *n* increases from 1 to 3. Yields are discussed in terms of termination mechanisms, transfer constants and polar and steric effects.

Quantitative relationships in the chain transfer reactions of solvents with readily polymerizable monomers were investigated some time ago and are fairly well understood.[3] When Dr. E. C. Ladd of this Laboratory discovered that some monomers which do not polymerize readily or give only short chains with free radicals nevertheless give good

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[1] This experimental work was presented at the Conference on Organic Reaction Mechanisms, University of Notre Dame, September 3–6, 1946.

[2] (a) General Electric Co., Waterford, N. Y.; (b) General Electric Research Laboratory, Schenectady, N. Y.

[3] (a) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); (b) R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948); (c) *Disc. Faraday Soc.*, **2**, 328 (1947); (d) F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948); (e) R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948).