

Radical Chain Halogenation Reactions of Chlorine Monoxide¹

Dennis D. Tanner and Nestor Nychka

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. Received July 25, 1966

Abstract: The reaction of carbon tetrachloride solutions of chlorine monoxide with substituted and unsubstituted alkanes has been shown to be a free-radical chain halogenation having the over-all stoichiometry: $2RH + Cl_2O \rightarrow 2RCl + H_2O$. The mechanism of the reaction is believed to proceed through a mixed chain involving OCl and chlorine radicals as the chain-propagating species. Although the selectivity of the reagent, as calculated from the product distribution of halogenation of unsubstituted hydrocarbons, is not as great as *t*-butyl hypochlorite, the isomer distribution for halogenation of substituted alkanes is almost identical with that of this more selective reagent.

The vigorous reaction of chlorine monoxide with organic materials is well known,² but for the studies of Goldschmidt and Schüssler³ and a recent communication by Phillips and Shaw⁴ no investigation of its halogenation reactions with saturated alkanes is reported in the literature. Goldschmidt and Schüssler noted that acetone and acetoacetic ester gave chlorination products with chlorine monoxide. More recently Phillips and Shaw have reported that the vapor-phase thermolysis of chlorine monoxide with propane at 100° yields isopropyl chloride and *n*-propyl chloride in a molar ratio of 7:1, and that these chlorides and hypochlorous acid are the sole products of the reaction. These observations apparently are only valid when the reaction is run to less than 40% completion. The isomer distribution found by Phillips and Shaw is not compatible with a mechanism whose product distribution is determined by chlorine radical abstraction, since the reaction of molecular chlorine and propane under similar conditions shows a ratio of primary to secondary products which approaches 1:1.⁵ Furthermore if one calculates the secondary to primary hydrogen selectivity, per hydrogen, a ratio of 21:1 is obtained, making chlorine monoxide one of the most selective chlorinating reagents available.

Because of its apparent high selectivity, a detailed study of the halogenation reactions of chlorine monoxide was undertaken not only for our interest in the theoretical aspects of the reaction but also to evaluate its utility as a synthetic reagent.

Discussion and Results

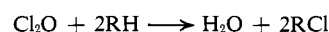
Irradiation at 40° of a dilute carbon tetrachloride solution of chlorine monoxide, 0.18 *M*, and a representative substrate, 1-chlorobutane, 1.8 *M*, results in the distribution of products seen in Table I. For each mole of chlorine monoxide, 2 moles of alkyl halide and 1 mole of water are produced. The small amount of hydrochloric acid found makes up a material balance for chlorine. The results for the other hydrocarbon

Table I. Products of the Photoinitiated Reaction of 1-Chlorobutane with 1 Mole of Chlorine Monoxide (1:10 Mole Ratio, 40°, CCl_4)

Products	Moles of product found ^a
1,1-Dichlorobutane	0.40 ± 0.01
1,2-Dichlorobutane	0.46 ± 0.01
1,3-Dichlorobutane	0.93 ± 0.02
1,4-Dichlorobutane	0.18 ± 0.003
HCl	0.06 ± 0.003
H ₂ O	0.97 ± 0.03

^a Reported values are average numbers from three or more independent experimental determinations.

halogenations studied are similar to those obtained for 1-chlorobutane and the over-all stoichiometry of the reaction is summarized by the following equation.



An example of the effect of reaction variables on the reaction rate of chlorine monoxide with 1-chlorobutane is shown in Table II. The induction period is counted

Table II. Reaction of 1-Chlorobutane and Chlorine Monoxide at 40° (0.18 *M* Chlorine Monoxide, 1.8 *M* 1-Chlorobutane)

Expt ^a	Induction period ^a	Reaction time ^a	Remarks
1	95	900 ^b	Dark, degassed
2	120	>3000 ^c	Dark, degassed, 0°
3	>5000	...	Dark, under oxygen
4	3	10	Photoinitiation, degassed
5	11	70	Photoinitiation, under oxygen
6	20	80	AIBN, ^d degassed
7	60	2000	AIBN, ^d under oxygen

^a Values reported are averages from three or more independent experiments. ^b Iodometric titration showed 2-3% of molecular chlorine present at reaction completion. ^c Iodometric titration showed the reaction to have proceeded about 40% in 3000 min. ^d AIBN concentrations were 0.02 mole % of those for chlorine monoxide. ^e In minutes.

from the time of equilibration, at 40°, to the time a visible change occurs, a fading of the brownish yellow color of chlorine monoxide in carbon tetrachloride and the first appearance of cloudiness owing to the precipitation of water. The reaction time is counted from equilibrium until the color of chlorine monoxide

(1) Presented in part at the 21st Annual Northwest Regional Meeting of the American Chemical Society, Vancouver, June 1966.

(2) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Suppl. II, part I, Longmans, Green and Co., London, 1956, p. 520.

(3) S. Goldschmidt and H. Schüssler, *Ber.*, **58B**, 566 (1925).

(4) L. Phillips and R. Shaw, *Proc. Chem. Soc.*, 294 (1962).

(5) J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959).

Table III. Isomer Distribution for 1-Chloropropane Halogenations (40°, Photoinitiated)

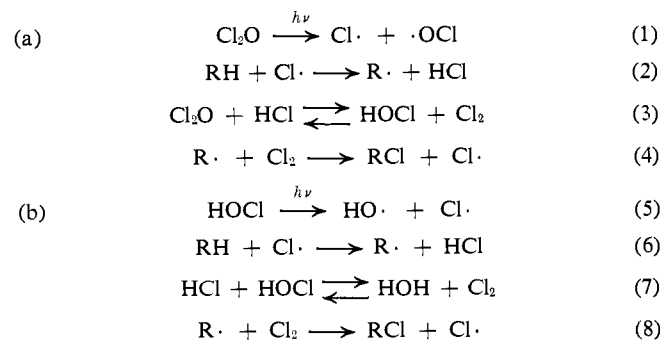
Reaction	Reagent	Solvent	Isomer distribution, % ^a		
			1,1	1,2	1,3
1	Cl ₂ O	CCl ₄	42.8 ± 0.7	42.4 ± 0.3	14.8 ± 1.1
2	Cl ₂ O	CCl ₄ -H ₂ O (100:1)	42.0 ± 1.5	42.0 ± 0.9	16.0 ± 0.4
3	HOCl	CCl ₄ -H ₂ O (10:1)	21.8 ± 0.4	46.9 ± 0.3	31.3 ± 0.2
4	HOCl	CCl ₄ -H ₂ O (1:1)	17.2 ± 0.4	49.2 ± 1.1	33.6 ± 1.6
5 ^b	HOCl	C ₃ H ₇ Cl-H ₂ O (1:1)	20	50	30
6	Cl ₂	CCl ₄	11.8 ± 0.7	57.6 ± 0.5	30.7 ± 0.3

^a Values are averages of the results of three or more independent experiments; errors are average deviations from the mean. ^b Results from single experiment only.

is discharged, at which time there is no titer as determined by iodometric titration. The reaction mixture is stable in the absence of light when it is inhibited by atmospheric amounts of oxygen (Table II, expt 3), but degassed samples under the same conditions undergo a slow "spontaneous" radical reaction (Table II, expt 1). The dark reaction at 40° is general also for unsubstituted hydrocarbons as demonstrated by the "spontaneous" reaction of cyclohexane and 2,3-dimethylbutane. The simplest explanation for the "uninitiated" reaction involves a very slow thermal decomposition of chlorine monoxide followed by a long-chain halogenation process, which can be inhibited by molecular oxygen, having the same mechanistic path as the photoinitiated reaction. The slow thermal initiation process is substantiated by the known thermal decomposition of chlorine monoxide in carbon tetrachloride at moderately higher temperatures⁶ and by the observed lengthening of the reaction time for the reaction of 1-chlorobutane at 0° (Table II, expt 2). The behavior of chlorine monoxide and an organic hydrocarbon is that predicted for radical chain halogenation: acceleration of the reaction rate by light (Table II, expt 4, 5) and AIBN in the absence of light (Table II, expt 6, 7), and inhibition by molecular oxygen (Table II, expt 3).

With a detailed analysis of the products of halogenation and the inhibition and initiation experiments a detailed mechanism for the reaction can be proposed and tested for.

The first chain mechanism proposed proceeds entirely by chlorine atom abstraction. In the sequence



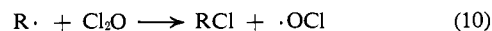
of reactions (eq 1-8) utilizing the precedented equilibrium reactions (3⁷ and 7²), abstraction of hydrogen,

(6) E. A. Moelwyn-Hughes and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A131**, 177 (1931).

(7) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., London, 1922, p 242.

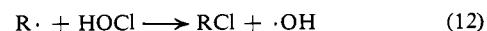
and thus determination of product distribution, proceeds solely by halogen atom abstraction.

Mechanism 2 involves, after initiation (1), the chain sequence (9 and 10). The hypochlorous acid produced



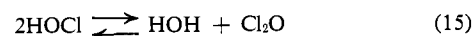
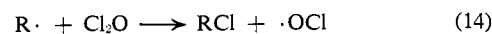
in (9) is subsequently utilized as in sequence b of mechanism 1 (5-8). In this mixed chain OCl and chlorine radicals are the abstracting species, and the combination of the reactivities of these two radicals give the reactivity that is observed.

The third mechanism poses an alternative radical chain to account for the consumption of hypochlorous acid produced by the series of reactions (1, 9, and 10).



This proposed series proceeds by a mixed chain where the abstracting radicals are $\cdot\text{OCl}$ and $\cdot\text{OH}$.

If the known equilibrium between chlorine monoxide in carbon tetrachloride and aqueous hypochlorous acid is involved (15),⁸ then yet another possible reaction chain can be postulated where the abstracting species is solely the OCl radical (1 and 13-15). The operation



of mechanism 4 must necessarily depend upon the ratio of the aqueous to organic phases and to the distribution coefficient between them as well as the timing of the sequence of reactions taking place.

In an attempt to differentiate between the four mechanisms proposed the relative reactivities for hydrogen abstraction of the hydrogen atoms in 1-chloropropane, 1-chlorobutane, and *n*-butyronitrile were examined. Comparison of the product isomer distributions for these substituted alkanes are sufficiently different from those obtained with molecular chlorine to clearly eliminate the possibility that mechanism 1, solely chlorine atom abstraction, was operative in these halogenations (see Tables III, IV, VI).

When a drop of water is initially added to the reaction in a concentration sufficient to convert the chlorine monoxide to hypochlorous acid, and the photolysis was carried out with continuous agitation of the mixture, the reactivity was not changed sufficiently to draw any mechanistic conclusions in comparing it with the reaction without added water (Table III, reaction 2;

(8) S. Goldschmidt, *Ber.*, **52B**, 753 (1919).

Table IV. Isomer Distribution for 1-Chlorobutane Halogenations^a (40°, Photoinitiated)

Reaction	Reagent	Solvent	Isomer distribution, %			
			1,1	1,2	1,3	1,4
1	Cl ₂ O	CCl ₄	21.6 ± 0.2	19.0 ± 0.1	50.8 ± 0.3	8.6 ± 0.3
2	Cl ₂ O	CCl ₄ -H ₂ O (100:1)	17.4 ± 0.5	21.0 ± 0.4	47.0 ± 1.0	14.6 ± 0.9
3	HOCl	CCl ₄ -H ₂ O (10:1)	7.8 ± 1.6	21.7 ± 2.1	47.1 ± 2.2	23.4 ± 1.7
4	HOCl	CCl ₄ -H ₂ O (1:1)	7.0 ± 0.1	23.2 ± 0.2	43.8 ± 0.1	26.0 ± 0.2
5 ^b	Cl ₂	Neat, 34° ^c	6.6	23.5	51.4	18.4

^a Results are average values from three or more independent experiments; errors are average of deviation from the mean. ^b Results from duplicate experiments only. ^c C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

Table IV, reaction 2). The equilibrium of chlorine monoxide with water, in carbon tetrachloride, a two-phase distribution, only lies to the side of hypochlorous acid when there is sufficient water present.^{8,9}

When aqueous hypochlorous acid which is free from molecular chlorine and chlorine monoxide is used, a two-phase reaction to photohalogenate the substituted alkanes (Table III, reactions 3, 4, and 5; Table IV, reactions 3 and 4), the product distribution is very similar to that of the reaction with molecular chlorine; however, this seems to be somewhat dependent on the ratio and nature of the organic and aqueous phases (Tables III and IV). Investigation of the products of chlorination of *n*-butane and 2,3-dimethylbutane with hypochlorous acid yields primary:secondary:tertiary hydrogen selectivity ratios which are experimentally indistinguishable from those reported in the literature for halogenation with molecular chlorine (see Table V).

Table V. Comparison of Selectivity between Chlorinating Reagents^a

Chlorinating agent	Selectivity		
	Primary	Secondary	Tertiary
Cl ₂ (27°) ^b	1	3.9	5.1
HOCl (40°, aqueous)	1	3.8 ± 0.3	4.6 ± 0.1 ^d
<i>t</i> -C ₄ H ₉ OCl (40°) ^c	1	8	44
Cl ₂ O (100°, vapor phase) ^d	1	21	...
Cl ₂ O	1	11.5 ± 0.3	24 ± 1 ^d

^a Values obtained from halogenation of 2,3-dimethylbutane and *n*-butane. ^b Values for gas-phase photochlorination: P. C. Anson, P. S. Fredericks, and J. M. Tedder, *J. Chem. Soc.*, 918 (1959). ^c C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960). ^d Errors are average deviation from the mean of three or more independent experiments. ^e See ref 4.

Selectivity values for chlorine monoxide obtained in the same manner as for hypochlorous acid are less than one-half as large as one would predict from the reported results of Phillips and Shaw⁴ (see Table V).

We can conclude from these experiments and from the results of Phillips and Shaw that the proposed mechanism involving only ·OCl abstraction is not the product-determining sequence of reactions, but that a mixed radical chain, mechanism 2, in which OCl radicals from chlorine monoxide and chlorine radicals from hypochlorous acid are the chain-propagating species, operates. This conclusion carries the reservation that hydroxyl radicals do not have the same reactivity and selectivity as do chlorine atoms.

(9) W. A. Roth, *Z. Physik. Chem.*, **A145**, 289 (1929).

Further evidence in support of the mixed radical chain, mechanism 2, is obtained from a study of the product distribution at various stages of progress during the reaction of 1-chloropropane with chlorine monoxide (Table VII). As the reaction proceeded either in the dark ("spontaneous" reaction) or by photoinitiation the isomer distribution changes from one indic-

Table VI. Comparison of the Isomer Distributions for the Halogenation of Substituted Alkanes with Several Chlorinating Agents (40°, Photoinitiation, CCl₄ Solvent)

Molecule	Reagent	Isomer distribution, %			
		1,1	1,2	1,3	1,4
1-Chlorobutane	Cl ₂ O	21.6	19.0	50.8	8.6
	<i>t</i> -C ₄ H ₉ OCl ^a	21.3	19.6	43.6	15.4
	Cl ₂ (34°, neat) ^b	6.6	23.5	51.4	18.4
1-Chloropropane	Cl ₂ O	42.8	42.4	14.8	
	<i>t</i> -C ₄ H ₉ OCl ^a (neat)	47.7	41.4	10.9	
<i>n</i> -Butyronitrile	Cl ₂	11.8	57.6	30.7	
	Cl ₂ O	...	20.1	38.9	41.0
	<i>t</i> -C ₄ H ₉ OCl ^a (neat)	...	22.4	43.7	33.9
	Cl ₂ ^c	...	0	69	31

^a C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6113 (1960). ^b C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959). ^c A. Bruylants, M. Tits, C. Dieu, and R. Gauthier, *Bull. Soc. Chim. Belges*, **61**, 266 (1952).

ative of the more selective ·OCl to a distribution in part determined by chlorine atom abstraction. The timing of the various reaction sequences can be inferred as proceeding by a buildup in the concentration of hypochlorous acid in the first part of the reaction. The spontaneous reaction varies somewhat in product distribution from the photoinitiated one in the later stages of the reactions progress. This can be rationalized on the basis of the equilibrium reaction 14. As the concentration of hypochlorous acid builds up in the dark reaction the equilibrium between hypochlorous acid and chlorine monoxide in carbon tetrachloride favors the formation of chlorine monoxide. The chlorine monoxide undergoes decomposition and gives chlorination products by the more selective ·OCl chain (*e.g.*, 9-10). The dark reaction would not go to >97-98% completion. The remaining 2-3% of the "active" chlorine present was found to be molecular chlorine, presumably formed by the reaction of hydrochloric acid with hypochlorous acid, *e.g.*, eq 7.

The halogenation of negatively substituted alkanes is an available method of investigating the selectivity and response to polar effects of the radical carrying

Table VII. Isomer Distribution of 1-Chloropropane at Various Stages in the Reaction with Chlorine Monoxide at 40°

% active Cl ₂ consumed	Time, min	Isomer distribution, %		
		1,1	1,2	1,3
25	10	60.9	33.5	5.6
32	6	60.1	33.7	6.2
35	27	60.1	33.8	6.1
49 ^a	1 5 ^b	59.1	33.9	7.0
50	90	59.2	34.4	6.4
59 ^a	23 ^c , 3 ^b	58.2	34.4	7.4
62 ^a	5 ^b	56.8	35.2	8.0
89	663	56.8	35.6	7.6
96	714	51.8	36.5	11.7
97	1200	50.7	36.9	11.4
98	5522	51.8	37.1	11.1
100 ^a	8 ^b	42.8	42.4	14.8

^a Reactions initiated by photolysis after equilibration at 40° in the dark. ^b Times indicating the photolysis time after 8-min equilibration in the dark at 40°. ^c After 23 min, this ampoule was slightly cloudy; then it was photolyzed for 3 min, the reaction was quenched by potassium iodide solution, and then the ampoule analyzed.

out the abstraction process.^{10,11} The combination of these effects represents the reactivity of the abstracting species. In Table VI a comparison is shown of the reactivity of chlorine monoxide, molecular chlorine, and the selective chlorinating reagent, *t*-butyl hypochlorite, with 1-chlorobutane, 1-chloropropane, and *n*-butyronitrile. Although the selectivity of chlorine monoxide is not as great as that of *t*-butyl hypochlorite (Table V) the reactivity of chlorine monoxide with substituted alkanes is almost identical with that of *t*-butyl hypochlorite.

Experimental Section

Materials. Chlorine monoxide was prepared by treating a dry carbon tetrachloride solution of chlorine with excess, dry, yellow mercuric oxide (B. D. H. Ltd. or Fisher Scientific Co., reagent grade) as described by Cady.¹² The resulting solution, approximately 0.18 *M* in chlorine monoxide, was stored in the dark, at 0°, in a glass-stoppered bottle. Before use, analysis by iodometric titration showed the solution to be free from molecular chlorine.¹² Ultraviolet spectrometry showed the chlorine monoxide solution not to be contaminated by hypochlorous acid.² All reactions were run with solutions which were completely chlorine free. The mercuric oxide was recovered for further use.¹²

Hypochlorous acid was prepared by shaking chlorine monoxide with water and extracting the aqueous layer.¹² Its purity was determined by iodometric titration, *i.e.*, determined to be free from molecular chlorine,¹² and its ultraviolet spectra showed it to be free from detectable amounts of chlorine monoxide.² Commercially available 1-chlorobutane was distilled, and its purity was checked by boiling point, refractive index, and gas chromatography (glpc). Phillips research grade *n*-butane and 2,3-dimethylbutane were used without further purification. All other substrates were commercially available materials whose purity was checked by glpc and used as obtained.

Carbon tetrachloride used as solvent was Fisher A.R. grade which was dried by distillation from phosphoric oxide; its purity was checked by glpc.

Chlorination of Substituted Alkanes. The reactions were carried out in sealed Pyrex ampoules which had been degassed by the freeze-thaw method. Experiments under oxygen were run in ampoules which contained atmospheric concentrations of oxygen. When irradiation was used to initiate the reaction, the light source was 2-200-w incandescent light bulbs. All reactions were run in a thermostated Pyrex water bath, 40.0 ± 0.2°. The average molarities of substrate to halogenating reagent were 1.8:0.18. The

tubes containing 2.5 to 4 ml of solution were equilibrated at 40° in the dark for 15 min, and then were subjected to light. Visually, the reaction commenced when a cloudiness developed and the brown-yellow color of chlorine monoxide gradually faded. The reaction was complete, an absence of active halogen,¹² when the ampoules were cloudy, colorless.

In the case of reactions with hypochlorous acid and reactions of chlorine monoxide run with added water, the ampoules were continually shaken during photolysis.

Analysis of the product mixtures was carried out by glpc using an Aerograph HY-FI Model 600-D equipped with a Model 328 temperature program controller. Peak areas were measured using a Model 201-B Disc integrator or by the method of peak height and half-height peak widths. Peak area ratios were taken as mole ratios. This approximation was valid since in cases where repetition of *t*-butyl hypochlorite experiments were carried out, the reported values could be duplicated within 2-3%. In 1-chlorobutane experiments used to determine product yields the values agree within 3% of the area ratio values.

1-Chlorobutane chlorination mixtures were analyzed using a 10 ft × 0.125 in. neopentyl glycol succinate (NPGS) column having Firebrick as the solid support. The four major product peaks were identified as the assigned isomers by direct comparison of their retention times with those of authentic commercially available samples. Two minor products were eluted just before the last product peak. These peaks account for approximately 2% of the total products. These minor products are most probably products of multichlorination, and no further work was done on them. Chlorination products were eluted in the order, 1,1-, 1,2-, 1,3-, and 1,4-dichlorobutane.

In the material balance experiments, all the isomer peaks were measured relative to an internal standard, Freon 112. Actual amounts were calculated from calibration plots of area ratios *vs.* mole ratios for Freon 112 *vs.* the authentic samples. The analysis of water was carried out by Karl-Fischer titration.¹³ The small amounts of hydrochloric acid were detected by holding moist litmus paper over the mouth of a newly opened ampoule and the amount of acid was determined by iodometric titration with standard sodium thiosulfate.¹²

1-Chloropropane chlorination products were analyzed on the 10 ft × 0.125 in. NPGS column. Two of the three product peaks were identified by their identical retention times on three columns with commercially available compounds. The 1,1-C₃H₇Cl₂ isomer was assigned by elimination since it was the only peak left unidentified on the chromatogram. A check on the assignment of the isomer peaks was made by repeating the halogenation experiments of Walling using *t*-butyl hypochlorite¹⁰ and comparing their assignments with ours. The chlorination products were eluted from the glpc column in the order 1,1-, 1,2-, and 1,3-dichloropropane.

The photochlorination of 1-chloropropane with molecular chlorine was carried out in the same way as the experiments with chlorine monoxide and with the same concentrations of chlorinating agent to substrate as was used in the chlorine monoxide halogenations.

***n*-Butyronitrile** reaction mixtures were analyzed by glpc using a 10 ft × 0.125 in. Carbowax 20M column having Chromosorb W as the solid support. Only three product peaks were observed. These products were identified by comparison of the known distribution of products resulting from the *t*-butyl hypochlorite reactions with *n*-butyronitrile.¹⁰ As a check on the assignments, the retention time of the commercially available 4-chlorobutyronitrile was compared with the assignment made from the *t*-butyl hypochlorite reaction. Elution order for the chlorination product was 2-, 3-, and 4-chlorobutyronitrile.

Chlorination of *n*-Butane and 2,3-Dimethylbutane. The primary:secondary:tertiary selectivity ratios were calculated from a comparison of product distributions in the usual manner.

***n*-Butane** chlorination products were analyzed on a 10 ft × 0.125 in. Ucon 50 HB 2000 polar on firebrick column. Only two products were observed. The structure of the 1-chlorobutane was assigned to its corresponding peak (second peak) on the gas chromatogram by comparison of its retention time by glpc with that of an authentic sample. The remaining peak was assigned the structure of the secondary halide.

2,3-Dimethylbutane chlorination products were analyzed by glpc on the 10 ft × 0.125 in. NPGS column. Two minor low-boiling products and two major higher boiling products were ob-

(10) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6113 (1960).

(11) H. Kloosterziel, *Rec. Trav. Chim.*, **82**, 508 (1963).

(12) G. H. Cady, *Inorg. Syn.*, **5**, 156 (1957).

(13) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

served. The minor products, 1–2%, were believed to be 2,3-dimethyl-2-butane and 2,3-dimethyl-1-butene, resulting from dehydrohalogenation of the tertiary halide during analysis. The 2,3-dimethyl-2-butene structure was assigned to its corresponding peak by comparison of its retention time with that of an authentic sample. The two major products, >98% of the products obtained, were assigned the structures 2-chloro-2,3-dimethylbutane and 1-chloro-2,3-dimethylbutane. The tertiary chloride was prepared by the method described by Shiner,¹⁴ and its retention time by glpc was found to be the same as that for the major isomer assigned that structure. The order of elution from the column was 2-chloro-2,3-dimethylbutane followed by 1-chloro-2,3-dimethylbutane.

(14) V. J. Shiner, *J. Am. Chem. Soc.*, **76**, 1603 (1954).

Chlorinations at Incomplete Reaction. After initial reaction, dark or photoinitiated (see Table VII), the reactions were quenched in liquid nitrogen and the ampoules broken under acidified potassium iodide and titrated for active chlorine.¹² After titration the carbon tetrachloride layer was extracted, and the organic material was analyzed by glpc as previously described. Repeated extractions of the organic phase and reanalysis of the product mixture assured us that the product distribution determination was not affected by the contact of the reaction mixture with water during the titration.

Acknowledgment. The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

The Kinetic Hydrogen Isotope Effects in the Bromination of Some Polyalkylbenzene Systems¹

Enrico Baciocchi, Gabriello Illuminati, Giancarlo Sleiter, and Franco Stegel

Contribution from the Department of Chemistry of the University of Rome, Rome, Italy. Received July 5, 1966

Abstract: The preparative, product analysis, and kinetic aspects for the determination of the kinetic hydrogen isotope effects, k_H/k_D , for the bromination of a number of polyalkylbenzene systems are described. The reaction is either bromination by molecular bromine in acetic acid and in nitromethane or silver ion catalyzed bromination in acetic acid–dioxane mixture (1,3,5-tri-*t*-butylbenzene). The isotope effect was found to be appreciably larger in nitromethane than in acetic acid solution (5-*t*-butylhemimellitene). Further evidence is presented in support of the view that steric hindrance at the reaction site is an important contributing factor for the occurrence of isotope effects in electrophilic aromatic substitution.

Since the first reports on the influence of steric hindrance on hydrogen isotope effects in electrophilic aromatic substitution^{2–4} there has been cumulative evidence on the generality of this phenomenon.^{5–9} More generally, the growing information on isotope effects for this reaction has been authoritatively discussed in recent reviews.¹⁰

In continuation of our studies in this field, we wish to report the results of a systematic investigation on the hydrogen isotope effects in the bromination of a number of polyalkylbenzenes characterized by a reaction center flanked by alkyl groups on both sides.

We also take this opportunity to include additional experimental information on the results reported in our previous reports.

Results

Except for 1,3,5-tri-*t*-butylbenzene (I), the hydrogen isotope effects were investigated for the dark bromination with molecular bromine under conditions for which the kinetics and mechanism of the reaction are fairly well known.¹¹ Anhydrous acetic acid and nitromethane were used as solvents depending on the reactivity of the substrate. Unlike mesitylene, the methylated analog, bromination in any of the latter conditions is exceedingly slow in the case of 1,3,5-tri-*t*-butylbenzene, which indicates a large steric hindrance effect upon the entrance of the halogenating species; therefore, the silver ion catalyzed bromination was used in this case.⁴

The hydrogen isotope effects, k_H/k_D , were evaluated from rate measurements in all cases except compound I. The course of the reaction was known from previous studies and had to be ascertained only with 5-*t*-butylhemimellitene that brominates smoothly with Br₂ to yield the 4-bromo derivative under conditions analogous to those adopted for the kinetics work.

- (1) Part XXII of the series: Substitution in Polymethylbenzenes.
- (2) H. Zollinger, *Experientia*, **12**, 165 (1956).
- (3) E. Baciocchi, G. Illuminati, and G. Sleiter, *Tetrahedron Letters*, No. 23, 30 (1960).
- (4) P. C. Myhre, *Acta Chem. Scand.*, **14**, 219 (1960).
- (5) P. G. Farrell and S. F. Mason, *Nature*, **197**, 590 (1963).
- (6) G. Illuminati and F. Stegel, *Ric. Sci. Rend., Sect. A*, **7**, 460 (1964); E. Baciocchi, G. Illuminati, and F. Stegel, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 158.
- (7) J. E. Dubois and R. Uzan, *Tetrahedron Letters*, No. 5, 309 (1965).
- (8) E. Helgstrand, *Acta Chem. Scand.*, **19**, 1583 (1965).
- (9) P. C. Myhre and M. Beug, *J. Am. Chem. Soc.*, **88**, 1569 (1966).
- (10) (a) H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 163 (1964); (b) E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 157 (1964); (c) G. A. Olah, *J. Tenn. Acad. Sci.*, **40**, 77 (1965).

- (11) (a) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworth and Co., Ltd., London, 1959, p 123; (b) E. Baciocchi and G. Illuminati, *Progr. Phys. Org. Chem.*, in press. (c) Bromination is known to involve terms that are of first, second, and higher order in bromine concentration. Under the conditions used here, the term second order in bromine is presumed to predominate and has been assigned the mechanism of eq 1, 2, and 3.