the acetate than that for the formate ester.[20] This result is also consistent with the structural effect on the entropy of solvation pictured by Humphreys and Hammett.[19] The possibility that the rate of methanolysis of the acetate is retarded relative to the formate by hyperconjugative stabilization in the ester[18] (as well as by the more electron-releasing inductive effect) is not eliminated, although perhaps it is rendered a less favored explanation by the observed difference in the entropies of activation.

The large negative entropies of activation observed in each case are consistent with the $B_{Ac}2$ mechanism, that is, are in accord with the entropy decrease expected for the addition of methoxide ion to the carbonyl group to form a transition state with a well-localized negative charge.

Appendix

The following procedure was used to determine the best fit of the data to equation 1. The problem is to find the parameters for a plane whose general equation is

$$y = b_1x_1 + b_2x_2 + b_0 \qquad (2)$$

The experimentally measured quantity is y, the variables are x_1 and x_2, and the correlation coefficients of these variables are b_0, b_1 and b_2. Following the method of "least squares" it is desired to find the values of b_0, b_1 and b_2 such that the sum of the squares of the vertical deviations of the measured values of y (n in number) from the regression plane are a minimum. The expressions for obtaining the correlation coefficients are given in terms of the quantities[21]

$$C_{11} = n\Sigma x_2^2 - (\Sigma x_2)^2$$
$$C_{12} = \Sigma x_1\Sigma x_2 - n\Sigma x_1x_2$$
$$C_{13} = \Sigma x_1x_2\Sigma x_2 - \Sigma x_1\Sigma x_2^2$$
$$C_{22} = n\Sigma x_1^2 - (\Sigma x_1)^2$$
$$C_{23} = \Sigma x_1\Sigma x_1x_2 - \Sigma x_1^2\Sigma x_2$$
$$C_{33} = \Sigma x_1^2\Sigma x_2^2 - (\Sigma x_1x_2)^2$$
$$D = C_{11}\Sigma x_1^2 + C_{12}\Sigma x_1x_2 + C_{13}\Sigma x_1$$

then

$$b_1 = \frac{1}{D}(C_{11}\Sigma x_1y + C_{12}\Sigma x_2y + C_{13}\Sigma y)$$

$$b_2 = \frac{1}{D}(C_{12}\Sigma x_1y + C_{22}\Sigma x_2y + C_{23}\Sigma y)$$

$$b_0 = \frac{1}{D}(C_{13}\Sigma x_1y + C_{23}\Sigma x_2y + C_{33}\Sigma y)$$

The standard deviations in the correlation coefficients are obtained in terms of the standard deviation of the entire correlation, δ^2, as obtained from

$$\delta^2 = \frac{\Sigma y^2 - b_1\Sigma x_1y - b_2\Sigma x_2y - b_0\Sigma y}{n - 3}$$

Then the standard deviation in b_1 is $(C_{11}/D)\ \delta^2$, in b_2 is $(C_{22}/D)\ \delta^2$, and in b_0 is $(C_{33}/D)\ \delta^2$. The multiple correlation coefficient, R, is obtained from the expression

$$R = \left[\frac{b_1\Sigma x_1y + b_2\Sigma x_2y + b_0\Sigma y - 1/n(\Sigma y)^2}{\Sigma y^2 - 1/n(\Sigma y)^2}\right]^{1/2}$$

In using the above relationships to obtain the best fit of the methanolysis rates to equation 1, several definitions are made

$$y = \log k,\ x_1 = \sigma^*,\ x_2 = E_s,\ b_0 = \log k_0,\ b_1 = \rho^*, \text{ and } b_2 = \delta$$

Acknowledgment.—The authors are indebted to Mr. Robert Nieman for determining the rate of alkaline saponification of ethyl cyanoacetate and to Mr. Richard A. Javick for determining the rate of the acid-catalyzed hydrolysis of this ester.

UNIVERSITY PARK, PENNA.

[20] R. W. Taft, Jr., THIS JOURNAL, **75**, 4534 (1953); *cf.* reference 11c, p. 665.

[21] R. L. Anderson and T. A. Bancroft, "Statistical Theory in Research," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, Chapt. 14.

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

γ-Ray Initiated Reactions.[1] I. The Addition of Bromotrichloromethane to Alkenes

BY EL-AHMADI I. HEIBA[2] AND LEIGH C. ANDERSON

RECEIVED AUGUST 20, 1956

The reaction of bromotrichloromethane with a number of alkenes under the effect of γ-rays is described. 1-Substituted alkenes gave 1:1 addition products of the general formula $R-CHBr-CH_2-CCl_3$, but cyclic alkenes revealed beside the 1:1 addition products the corresponding 1,2-dibromo- and the 1,2-ditrichloromethyl compounds. The 1,1-disubstituted alkene, α-methylstyrene, gave a dimer of the general formula $[Cl_3CCH_2CRR'-]_2$ in addition to the 1:1 addition product. 1,2-Disubstituted alkenes gave poor yields of the 1:1 addition product; with 1,2-dibromoethene, equimolecular quantities of $Cl_3C-CH{=}CHBr$ and $CHBr_2CHBr_2$ were the only products isolated.

The addition of bromotrichloromethane to unsaturated compounds under the influence of ultraviolet light or initiated with peroxides has been studied by previous investigators. This work presents data obtained from studies of similar reactions at room temperature, using γ-radiation from a 3.5 kilo-curie Co^{60} source as the activating agent. With a number of alkenes the products obtained with γ-radiation were the same as those formed with ultraviolet radiation or peroxides, but under the conditions used in this work there were a number of different reactions observed.

Octene-1, indene, butene-2, allyl chloride, allyl cyanide, ethyl cinnamate and *cis*- and *trans*-1,2-dichloroethene gave 1:1 addition products, as obtained with ultraviolet and peroxide initiators.

Kharasch and Friedlander[3] noted that there was little reaction between bromotrichloromethane and

[1] These studies were supported by Michigan Memorial Phoenix Project No. 98 given by the Chrysler Corporation. Some assistance was obtained from Atomic Energy Commission contract No. AT(11-1)-162 under the joint supervision of Leigh C. Anderson and Joseph J. Martin of the Department of Chemical Engineering.

[2] Study in leave from the Department of Chemistry, Faculty of Science, A'in Shams University, Cairo, Egypt.

[3] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

styrene at 20° under the influence of ultraviolet light, but a rapid reaction ensued when the temperature was raised to 50°. Under the influence of γ-rays, a 40% yield of the 1:1 addition product was obtained at 11°. On the other hand, α-methylstyrene, which has been shown[4] to be 4.2 times more reactive than styrene toward the trichloromethyl radical at 90° in the presence of ultraviolet light, showed a lower relative reactivity when γ-rays were used to induce the chain reaction at room temperature; it gave a yield of only 15.1% of the 1:1 addition product, in addition to the dimer 1,1,1,6,6,6-hexachloro-3,4-dimethyl-3,4-diphenylhexane.

The 1,2-disubstituted ethenes were remarkably unreactive[5] toward the bromotrichloromethane, *e.g.*, 1,2-dichloroethene and ethyl cinnamate[6] gave very poor yields of the 1:1 addition products and when the 1,2-disubstituents were phenyl, *e.g.*, *trans*-stilbene, the bromotrichloromethane failed to react.

The reaction of bromotrichloromethane with cyclic alkenes yielded, beside the 1:1 addition products, other types of compounds including in the case of cyclohexene, 1,2-di-(trichloromethyl)-cyclohexane, 2-bromocyclohexene and 1,2-dibromocyclohexane and with cyclopentene, 1,2-dibromocyclopentane and hexachloroethane. 1,2-Dibromoethene did not give a 1:1 addition product with bromotrichloromethane as 1,2-dichloroethene did but gave a small yield of equimolecular quantities of 1-bromo-3,3,3-trichloropropene and *sym*-tetrabromoethane. The formation of these products involves a type of displacement reaction which has not been reported previously.

Discussion

The tetrahaloalkanes that are obtained from the corresponding alkenes and bromotrichloromethane are believed to be formed by a mechanism previously reported by Kharasch[7] and co-workers.

$$\mathrm{BrCCl_3} \longrightarrow \mathrm{Br\cdot} + \cdot\mathrm{CCl_3} \qquad (1)$$

$$\mathrm{R{-}CH{=}CH_2} + \cdot\mathrm{CCl_3} \longrightarrow \mathrm{R{-}\dot{C}H{-}CH_2CCl_3} \qquad (2)$$

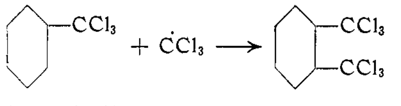
$$\mathrm{R{-}\dot{C}H{-}CH_2CCl_3} + \mathrm{BrCCl_3} \longrightarrow \mathrm{R{-}CHBr{-}CH_2CCl_3} + \cdot\mathrm{CCl_3} \qquad (3)$$

Table I presents a summary of the data obtained in this work. If one accepts the findings of Melville, *et al.*,[8] that the bromine transfer constant in reaction 3 does not show much variation from one system to another, then the order of reactivity of alkenes toward the trichloromethyl radical would be determined by the relative yield of the 1:1 addition product. On this assumption, our data would indicate the following order of reactivity: allyl cyanide > octene-1 > indene > cyclohexene, cyclopentene > allyl chloride > styrene >> α-methylstyrene > 1,2-dichloroethene > ethyl cinnamate.

The low reactivity of styrene with bromotrichloromethane under the influence of ultraviolet light at 20° was interpreted[3] by Kharasch and coworkers as resulting from the relative stability of the 1-phenyl-3,3,3-trichloropropyl radical formed by the preferential addition of trichloromethyl radical to the styrene double bond; the bromine transfer (reaction 3) was then concluded to be a slow reaction.

The relatively high yield of the styrene–bromotrichloromethane addition product obtained when γ-rays are used to induce the chain reaction does not support Kharasch's explanation and suggests that under these conditions the bromine transfer step did not proceed at a slow rate. Melville and co-workers[8] arrived at the same conclusion. This might be due to a higher excitation of the 1-phenyl-3,3,3-trichloropropyl radical by the high energy level radiation like a γ-ray or might be due to the high rate of initiation of bromotrichloromethane in the presence of such radiation. Careful fractionation of the reaction products failed to reveal the presence of a dimer of the 1-phenyl-3,3,3-trichloropropyl radical, a product which Mayo[9] isolated from the reaction of carbon tetrachloride and styrene in the presence of peroxides.

Contrary to the greater reactivity which was observed in the case of the γ-ray initiated reaction with styrene, α-methylstyrene showed a lower reactivity toward the trichloromethyl radical. This was indicated by the low yield of the 1:1 addition product and the isolation of the dimer 1,1,1,-6,6,6-hexachloro-3,4-dimethyl-3,4-diphenylhexane. The formation of *trans*-1,2-di-(trichloromethyl)-cyclohexane as determined by its hydrolysis to *cis*-1,2-dicarboxycyclohexane may be explained through a crossed termination reaction[10] that involves combination of a trichloromethyl radical and a monosubstituted cyclohexenyl radical.



(4)

Recently a similar type of reaction has been reported[11] from the reaction of iodotrifluoromethane with perfluorocyclohexene in the presence of ultraviolet light. The yield of 1,2-di-(trichloromethyl)-cyclohexane varied considerably when the intensity of the γ-ray dose rate was changed while the total dose was kept constant. Thus at a total dose of 4,000,000 R.E.P. the yield of this compound was raised from 2.5% at a dose rate of 80,000 R.E.P. per hour to 12.3% at a rate of 800,000 R.E.P. per hour. These data support the idea[12] that this type of termination reaction could be due to the presence of appreciable quantities of both trichloromethyl radical and hydrocarbon radical.

Cyclopentene, indene and octene-1, which add bromotrichloromethane readily, did not yield di-

---

[4] M. S. Kharasch, E. Simon and W. Nudenberg, *J. Org. Chem.*, **18**, 329 (1953).

[5] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 261 (1950).

[6] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

[7] M. S. Kharasch, Otto Reinmuth and W. H. Urry, THIS JOURNAL, **69**, 1105 (1947).

[8] W. H. Melville, F. C. Tutton and R. C. Robb, *Disc. Faraday Soc.*, **14**, 232 (1953).

[9] F. R. Mayo, THIS JOURNAL, **70**, 2561 (1948).

[10] (a) C. W. Walling, *ibid.*, **70**, 2561 (1948); **71**, 1930 (1949); (b) H. W. Melville and L. Valentine, *Proc. Roy. Soc.* (*London*), **200**, 337 (1950); (c) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); (d) H. W. Melville, F. C. Robb and R. C. Tutton, *Disc. Faraday Soc.*, **14**, 150 (1953).

[11] R. N. Haszeldine and F. E. Osborne, *J. Chem. Soc.*, 61 (1956).

[12] F. M. Lewis and F. R. Mayo, THIS JOURNAL, **76**, 457 (1954).

Table I

The Addition of $BrCCl_3$ to Alkenes Initiated by γ-Rays

Alkene	Products isolated	Time, hr.	Yield,[i] %	B.p.		M.p., °C.	Analyses, % Calcd.			Found		
				°C.	Mm.		C	H	Hal.[j]	C	H	Hal.
Cyclohexene		48										
	3-Bromocyclohexene[a]		12.3	64–65	15							
	cis-1,2-Dibromocyclohexane		8.3	52–53	1.5							
	1,2-Di-(trichloromethyl)-cyclohexane[b]		2.5	62–63	0.2	102	30.38	3.16	66.46	30.41	3.18	65.47
	*2-Bromo-1-trichloromethylcyclohexane[c]		63.5	71–73	.2		30.0	3.56	66.44	30.11	3.62	66.26
Cyclopentene		48										
	1,1-Dibromocyclopentane		9.8	72–73	14							
	Hexachloroethane					187						
	*2-Bromo-1-trichloromethylcylopentane[c]		61.8	60–63	0.8	−3	27.0	3.0	70	27.54	3.17	69.34
Indene		48										
	3-Bromo-2-trichloromethylindane[d]		78.5	112–113	.5	33	38.37	2.53	59.11	38.34	2.51	59.11
Octene-1		48										
	1,1,1-Trichloro-3-bromononane[e]		86	74	1.2							
Ethyl cinnamate		116										
	*Ethyl-β-bromo-α-trichloromethyldihydrocinnamate		4.7	110	0.1	67	38.45	3.2	49.79	38.34	3.20	49.68
1,2-Dichloroethene		65										
	1-Bromo-1,2,3,3,3-pentachloropropane		13.8	51	.1		12.18	0.68	87.14	12.26	0.84	86.98
Styrene		40										
	*1-Bromo-1-phenyl-3,3,3-trichloropropane[e]		39.1	92–94	.4	55						
α-Methylstyrene		65										
	*2-Phenyl-4,4,4-trichloro-1-butene[f]		15.1	80	.6		50.13	3.82	45.22	50.45	4.08	44.40
	3,4-Dimethyl-3,4-diphenyl-1,1,1,6,6,6-hexachlorohexane[g]		0.8			172	50.74	4.43	44.91	50.75	4.23	45.0
Allyl chloride		65										
	*2-Bromo-1,4,4,4-tetrachlorobutane[e]		82	56–57	.5							
Allyl cyanide		42										
	*3-Bromo-5,5,5-trichloropentanonitrile[h]		82	87	.5	15	22.94	2.07	70.11	22.6	1.89	70.24
Allyl bromide		48										
	1,2,3-Tribromopropane		48	46	.6	16						
	*3-Bromo-1,1,1,5,5,5-hexachloropentane		44	85	.5		16.81	1.40	81.79	16.43	1.43	82.09
1,2-Dibromoethene		65										
	1-Bromo-3,3,3-trichloropropene		15.5	75	25		16.04	0.89	83.07	16.07	0.91	83.14
	sym-Tetrabromoethane		17	51	0.3							

* Previous analyses reported for halogen only. [a] The identity of this substance was proved by identity of its infrared spectrum with that of an authentic sample; H. W. Grossley, *J. Chem. Soc.*, **85**, 1422 (1906); N. Zelinsky and A. Corsky, *Ber.*, **44**, 2315 (1911). [b] The substance crystallized as colorless prisms from petroleum ether 60–75°; mol. wt. calcd. 316, found 319. [c] For comparison see ref. 3. [d] Reference 3 reported an oil, $n^{20}D$ 1.6001. The structure was confirmed by acid hydrolysis to indene-2-carboxylic acid m.p. 234°. [e] Reference 7. [f] The 1:1 addition product lost one molecule of HBr during distillation, the ultraviolet absorption spectrum showed a maximum at 240 mμ, ϵ_{max} 8000; mol. wt. calcd. 235, found 231 (see ref. 4). [g] The substance was isolated from the reaction mixture by petroleum ether after distilling of the excess $BrCCl_3$ and α-methylstyrene. The solid that precipitated crystallized from benzene in colorless prisms. [h] The 1:1 addition product was characterized by its N analysis (ref. 6). The structure was confirmed by its acid hydrolysis to glutaconic acid (C. R. Ingold and T. F. Thorpe, *J. Chem. Soc.*, **119**, 499 (1921)). [i] Yield based on total alkene used. [j] Halogen for compounds containing both Br and Cl. Calculated from Ag equivalent as $BrCl_3$ addition compounds.

(trichloromethyl) compounds as in the case of cyclohexene. The predominating termination reaction appeared to be the dimerization of trichloromethyl radical.

$$2 \cdot CCl_3 \longrightarrow CCl_3\text{-}CCl_3 \qquad (5)$$

These observations suggest that not only the concentrations of the trichloromethyl and the alkene radicals but also the structure of the alkene free radical intermediate play a part in such crossed termination reactions.

1,2-Dibromocyclohexane gave 1-bromocyclohexene on dehydrohalogenation with alcoholic potassium hydroxide.[13] From available information concerning this elimination reaction[14a] and by assuming *trans* elimination in base-promoted dehydrohalogenation,[14b] *cis* configuration should be assigned to the dibromide.

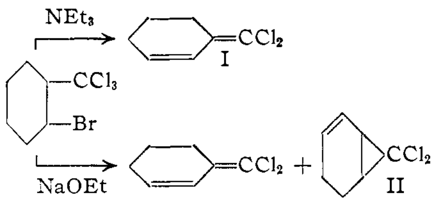
2-Bromo-1-trichloromethylcyclohexane is a fairly stable compound that was not decomposed during distillation and even when refluxed for 6 hours with triethylamine was only partially dehydrohalogenated to yield 3-dichloromethylenocyclohexene[3] (I), an observation that would not be expected from a *trans* isomer.[15] Dehydrohalogenation with sodium ethoxide yielded beside I another isomer whose reaction indicated that it might be 7,7-dichloro[4.1.0]-Δ^2-bicycloheptene [II].

---

[13] H. L. Goering, P. I. Abell and B. F. Aycock, This Journal **74**, 3588 (1952).

[14] (a) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941); (b) S. J. Cristol, This Journal, **69**, 338 (1947).

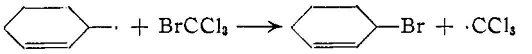
[15] H. L. Goering and H. Espy, *ibid.*, **77**, 5023 (1955).



The ultraviolet spectrum of I showed a maximum absorption at 250 mμ, Σ_{max} 12,200, which is characteristic for a conjugated diene structure; the spectrum of II, however, failed to show the presence of such a system and its infrared spectrum exhibited bands at 1610, 1000 and 860 cm.$^{-1}$.

The formation of 2-bromocyclohexene seems to be analogous to the allylic substitutions observed by other investigators[16] who used carbon tetrachloride as a solvent for cyclohexene and obtained the 3-chloro derivative in the presence of peroxides. The corresponding mechanism with bromotrichloromethane would be

(6)



(7)

The ease with which reaction 6 proceeds to give rise to the cyclohexenyl radical suggests that bromotrichloromethane could serve as an excellent brominating agent in some instances. Bromotrichloromethane has been found to brominate selectively the α-carbon of an aromatic side chain.[17]

Experimental[18]

In a typical experimental run, 0.25 mole of the alkene and one mole of bromotrichloromethane were mixed in a tube. A stream of dry nitrogen was allowed to bubble through the solution for 0.5 hour to free from oxygen and the tube was then sealed. After being irradiated for 48 hours at a rate of 81,000 R.E.P. per hour at room temperature that varied between 8–15°, the tube was opened, the unreacted bromotrichloromethane was removed under reduced pressure (60 mm.) and the residual products were subjected to repeated fractionation under vacuum.

Hydrolysis of 2-Bromo-1-trichloromethylcyclohexane.—2-Bromo-1-trichloromethylcyclohexane (5 g.) was vigorously stirred with 95% sulfuric acid (15 g.) while being heated in an oil-bath at 105–110°. When hydrogen chloride gas ceased to evolve (1.5 hours), the reaction mixture was poured onto ice, extracted with ether and then separated in the usual manner. A viscous brown material (1.7 g.) that crystallized from petroleum ether in colorless rosettes of needles was isolated, m.p. 110–111°. There was no depression of the melting point on admixture with an authentic sample[19] of *trans*-2-bromo-1-cyclohexanecarboxylic acid.

Dehydrohalogenation of 2-Bromo-1-trichloromethylcyclohexane. (1) **With Sodium Ethoxide.**—Sodium metal (4.6 g.) dissolved in absolute ethanol (50 ml.) was added in a dropwise manner to an alcoholic solution of 2-bromo-1-trichloromethylcyclohexane (28 g.) at a temperature of 40°. The reaction mixture was kept at this temperature while stirring for 2 hours after which it was decomposed with cold water and extracted with ether. Upon evaporation of the ether solvent and repeated fractional distillation of the residual oil under vacuum, the following fractions were collected. (a) A colorless oil (6.3 g.), b.p. 56–57° (1.8 mm.), n^{20}D 1.5320. The analysis of the substance was indicative of 3-dichloromethylenecyclohexene. *Anal.* Calcd. for $C_7H_8Cl_2$: Cl, 43.56. Found: Cl, 43.12. The ultraviolet absorption spectrum showed a maximum absorption at 250 mμ, Σ_{max} 12,200 (reported[3] λ_{max} 250 mμ, Σ_{max} 12,200).

(b) A colorless oil (4.8 g.), b.p. 64–65° (1.8 mm.), n^{20}D 1.5068. *Anal.* Calcd. for $C_7H_8Cl_2$: Cl, 43.56. Found: Cl, 44.11. There was no band characteristic of the conjugated diene system in the ultraviolet spectrum. The infrared spectrum exhibited bands at 1610, 1000 and 860 cm.$^{-1}$. On the basis of the above data, the substance was thought to be 7,7-dichloro[4.1.0]-Δ^2-bicycloheptene.

(c) Starting material (3.6 g.), b.p. 74° (0.2 mm.), n^{20}D 1.5470.

(2) **With Triethylamine.**—Cyclohexene–bromotrichloromethane addition product (36 g.) was refluxed with triethylamine for 10 hours. The reaction mixture was poured into water, extracted with ether and the extract was washed with 5% sulfuric acid to free it from the amine. The solvent was distilled off and the residue was fractionated under reduced pressure. (a) Colorless oil (5.2 g.), b.p. 57° (1.8 mm.), n^{20}D 1.5320. The substance was 3-dichloromethylenecyclohexene as obtained from sodium ethoxide dehydrohalogenation. (b) Starting material (25 g.), b.p. 73° (0.2 mm.), n^{20}D 1.5470.

Hydrolysis of 1,2-Di-(trichloromethyl)-cyclohexane.—The solid fraction which melted at 100–101° (2 g.) and which was obtained from the reaction of bromotrichloromethane and cyclohexene was stirred vigorously with 95% sulfuric acid (10 g.), while heating in an oil-bath at 110° for 2 hours. The dark brown solution was poured onto crushed ice (50 g.) and warmed at 50° on a steam bath for 0.5 hour. On cooling, *trans*-1,2-dicarboxycyclohexane (0.6 g.) was obtained. The acid crystallized in leaflets from water, m.p. 218–220°; it did not depress the melting point of an authentic sample.[20]

Preparation of 2-Bromocyclopentane-1-carboxylic Acid.—2-Bromo-1-trichloromethylcyclopentane (12 g.) was hydrolyzed with 95% sulfuric acid (40 g.) at 95–100° until hydrogen chloride gas ceased to be evolved. The dark brown reaction mixture was diluted with water and ether extracted. Evaporation of the ether left a semi-solid material that crystallized in colorless prisms from petroleum ether. The product which melted at 58° appears to be the *trans* isomer.

Anal. Calcd. for $C_6H_9O_2Br$: C, 37.3; H, 4.66; Br, 40.93; neut. equiv., 193. Found: C, 37.6; H, 4.87; Br, 40.72; neut. equiv., 192.6.

3-Bromo-5,5,5-trichloropentanamide.—3-Bromo-5,5,5-trichloropentanonitrile (2 g.) was hydrolyzed with 90% sulfuric acid (30 g.) while stirring and heating at 90° for two hours. The amide crystallized from hot water in colorless crystals, m.p. 116–117°. The infrared spectrum exhibited bands at 3360, 2900 and 1720 cm.$^{-1}$.

Anal. Calcd. for $C_5H_7Cl_3BrON$: C, 21.23; H, 2.46; hal, 65.78; N, 4.95. Found: C, 21.07; H, 2.47; hal, 65.87; N, 4.98.

3-Bromo-5,5,5-trichloropentanoic Acid.—The acid amide (1 g.) from above was refluxed with 50% hydrochloric acid for 2 hours, diluted with water and ether extracted. Evaporation of the dried ether left a solid that crystallized from petroleum ether (30–40°) in colorless prisms, 0.6 g., m.p. 66°.

Anal. Calcd. for $C_5H_6Cl_3O_2Br$: C, 21.08; H, 2.10; hal, 65.54; neut. equiv., 284.5. Found: C, 20.99; H, 2.09; hal, 65.44; neut. equiv., 283.

Ethyl 5,5,5-Trichloro-2-pentenoate.—A solution of 3-bromo-5,5,5-trichloropentanonitrile (13.2 g.) and absolute ethanol (150 ml.) saturated with hydrogen chloride was refluxed for 2.5 hours. The reaction mixture was cooled, diluted with water and extracted with ether. The ether extractions were washed with dilute alkali and dried over anhydrous sodium sulfate. The solvent was evaporated and the residual oil (9.8 g.) was distilled under vacuum, b.p. 74° (1.5 mm.), n^{24}D 1.4925. The expected β-bromoacid appeared to be unstable and lost one molecule of hydrogen bromide during the operation.

Anal. Calcd. for $C_7H_9Cl_3O_2$: C, 36.28; H, 3.88; Cl, 45.0. Found: C, 35.97; H, 3.87; Cl, 45.16.

5,5,5-Trichloro-2-pentenoic Acid.—The above ester (4 g.)

---

[16] (a) E. C. Kooyman and E. Farenhorst, *Rec. trav. chim.*, **70**, 867 (1951); (b) S. Israelashvili and J. Shabatay, *J. Chem. Soc.*, 326 (1951).

[17] Unpublished work.

[18] All melting points and boiling points are uncorrected. Analyses were made by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

[19] E. T. Boaman and R. P. Linstead, *J. Chem. Soc.*, 261 (1935).

[20] R. Stoermer and H. J. Steinbeck, *Ber.*, **65**, 413 (1932).

was refluxed with 50% hydrochloric acid for 4 hours. The reaction mixture was worked up in the usual manner for isolation of an acid. A solid acid (1.8 g.) which crystallized in flat prisms was obtained, m.p. 83°. The infrared spectrum exhibited bands at 1690 and 1610 cm.$^{-1}$.

Anal. Calcd. for $C_5H_5Cl_3O_2$: C, 29.48; H, 2.46; Cl, 52.3; neut. equiv., 203.5. Found: C, 29.53; H, 2.53; Cl, 52.29; neut. equiv., 202.

5,5-Dichloro-2,4-pentadienonitrile.—3-Bromo-5,5,5-trichloropentanonitrile (27 g.) was heated in an oil-bath at 180° for 2 hours until hydrogen halide gases ceased to evolve. The brownish material was extracted with ether, the extract washed with dilute aqueous sodium hydroxide and dried over anhydrous sodium sulfate. Upon evaporating the ether and distilling the residual oil under reduced pressure, 11.8 g. of material was obtained as colorless oil, b.p. 41–42° (0.2 mm.); cooling at 0°, the substance crystallized in long prismatic crystals, m.p. 16°, n^{23}D 1.5590. The ultraviolet spectrum showed a maximum absorption at 268 mμ, Σ_{max} 23300.

Anal. Calcd. for $C_5H_3Cl_2N$: C, 40.54; H, 2.02; Cl, 47.97; N, 9.45. Found: C, 40.43; H, 2.12; Cl, 48.04; N, 9.49.

5,5-Dichloro-2,4-pentadienoic Acid.—5,5-Dichloro-2,4-pentadienonitrile (3 g.) was refluxed with 50% hydrochloric acid (10 ml.) for 4 hours. The reaction mixture was allowed to cool, diluted with water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated. Long colorless needles (2.29 g.) were obtained from petroleum ether, m.p. 128°. The ultraviolet spectrum of the substance showed a maximum absorption at 268 mμ, ϵ_{max} 25000.

Anal. Calcd. for $C_5H_4Cl_2O_2$: C, 35.92; H, 2.38; Cl, 42.51; neut. equiv., 167. Found: C, 36.01; H, 2.40; Cl, 42.64; neut. equiv., 167.9.

Identification of the Products from the Reaction of 1,2-Dibromoethene with Bromotrichloromethane.—The fraction b.p. 75° (25 mm.), n^{27}D 1.5350 (of Table I) gave the analysis for 3-bromo-1,1,1-trichloropropene. The infrared spectrum exhibited bands at 3040 and 1740 cm.$^{-1}$. The structure was confirmed by ozonolysis. Decomposition of the ozonide with water and treatment of the resulting solution with 2,4-dinitrophenylhydrazine yielded a hydrazone which identified chloral. The infrared spectrum of the fraction b.p. 51° (3 mm.) was identical with that of an authentic sample of *sym*-tetrabromoethane.

Ann Arbor, Michigan

[A Joint Contribution from Oak Ridge National Laboratory, and The Physical Chemistry Laboratory, Oxford University]

Studies Involving Isotopically Labelled Formic Acid and its Derivatives.[1] II. Relation of the Absolute Reaction Rates to the Magnitudes of the Isotope Effects in the Oxidation of Formic-C^{13} Acid by Halogen Atoms

By Gus A. Ropp,[2a] C. J. Danby[2b] and D. A. Dominey[2c]

Received April 15, 1957

For two reactions of formic-C^{13} acid in which the rate steps involve extraction of hydrogen by halogen atoms, the rate isotope effects, k_{12}/k_{13}, have been carefully evaluated by methods involving mass spectrometric analysis of carbon-13 dioxide. The difference between the measured values of k_{12}/k_{13} for the two reactions has been found to be in the direction that the slower reaction shows the greater degree of isotope fractionation. This principle which has also been noted in earlier studies is discussed in terms of the possible residual carbon-to-hydrogen bonding to be expected in the activated states for the two reactions.

A. Introduction

The reported studies of isotope effects in organic reactions now number in the hundreds. Even the reviews and summaries are so numerous that general references to them here would be more confusing than enlightening. However, most of the research in this field is intended to (a) elucidate a reaction mechanism by comparing qualitatively or semi-quantitatively a measured isotope fractionation ratio with the ratio predicted from a possible mechanism of the reaction, or (b) explore the validity of some aspects of reaction rate theory by comparing—usually quantitatively—measured isotope fractionation factors with those which reaction rate theory would predict for a reaction whose rate step is understood. For studies of type (a), a mere qualitative reply as to whether isotope fractionation *does* or *does not* occur in a given instance is often sufficient to give the desired information about the reaction mechanism. It is in investigations of type (b), where quantitative correlation of experimental and theoretical values of isotope fractionation factors is usually sought, that the greatest difficulties arise. Granted that excellent work[3] has been done in developing from absolute reaction rate theory approximate expressions from which theoretical values of the isotope effect can, in principle, be calculated from spectroscopic data, the fact remains that the application of these expressions has been usually a matter of guesswork for all except the very simplest of reacting systems. Even on the experimental side many difficulties[4] arise and undoubtedly some questionable experimentally measured isotope fractionation factors have been reported.

It is believed that much useful information from experiments of type (b) might be obtained and several of the difficulties referred to above might be cancelled out by making comparative studies of the fractionation factors for a series of reactions all employing the same labeled reactant, formic acid. This molecule can be specifically labeled at either the carbon or oxygen atoms or in either position of the hydrogen atoms, and the various types of isotope effects might be correlated either within a

---

[1] An initial study of isotope fractionation in a formic acid reaction was reported by Gus A. Ropp, A. J. Weinberger and O. K. Neville, This Journal, **73**, 5573 (1951).

[2] (a) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.; (b) Physical Chemistry Laboratory, Oxford University, Oxford, England; (c) Balliol College, Oxford University, Oxford, England.

[3] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); Henry Eyring and F. W. Cagle, Jr., *J. Phys. Chem.*, **56**, 65 (1952).

[4] Gus A. Ropp, *J. Chem. Ed.*, **34**, 60 (1957).