servation. The angular positions of the maxima and minima of these quantities can be used to determine the particle radius. These methods extend the number of optical methods now available to four, the others being the spectral orders and transmission methods.

The determination of the concentrations of the components of a mixture of three monodispersed sols are amenable to practical treatment.

The effect of polydispersity on the higher order Tyndall spectra has been discussed and theoretical calculations have been made to show the effect of increasing the size distribution. An analysis utilizing the polarization ratio data indicates that the scattering properties of the sulfur sols prepared according to the methods developed in this Laboratory are similar to those with uniform distributions whose limits differ from the median by 5 to 10%.

Stokes parameters have been utilized to set up a criterion for monodispersity. A monodispersity factor P has been defined which will have the value 1 for an absolutely monodispersed system and a value less than 1 for a polydispersed system. Measures of monodispersity factors have been presented for several sols. The values of P are less than 1 but the range of values indicates that the sols are within the size distribution limits determined by the polarization ratio method. The latter method is superior for determination of the extent of size distribution although the monodispersity factor is a valuable and useful criterion of absolute monodispersity.

NEW YORK 27, N. Y. RECEIVED OCTOBER 8, 1949

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

The Peroxide-Induced Exchange of Hydrogen and Chlorine between Saturated Hydrocarbons and Polychloroalkanes[1]

BY JAMES P. WEST AND LOUIS SCHMERLING

When a saturated hydrocarbon is treated with certain polyhalogenated hydrocarbons in the presence of a catalytic amount of a decomposing organic peroxide, hydrogen–halogen exchange occurs and the hydrocarbon is converted to a monohaloalkane. Thus, for example, the reaction of isobutane with carbon tetrachloride in the presence of di-*t*-butyl peroxide at 130–140° results in the formation of *t*-butyl chloride and chloroform. The reaction presumably is a chain reaction

$$\mathrm{R'OOR'} \longrightarrow 2\mathrm{R'O}\cdot \ (e.g., \mathrm{R'} = t\text{-}\mathrm{C_4H_9} \text{ or } \mathrm{C_6H_5CO}) \qquad (1)$$

$$\mathrm{R'O}\cdot + \mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{R'OH} \qquad (2)$$

$$\mathrm{R}\cdot + \mathrm{CCl_4} \longrightarrow \mathrm{RCl} + \mathrm{Cl_3C}\cdot \qquad (3)$$

$$\mathrm{Cl_3C}\cdot + \mathrm{RH} \longrightarrow \mathrm{Cl_3CH} + \mathrm{R}\cdot \qquad (4)$$

The alkyl radical formed as in step 4 begins a new cycle as in step 3. Chain-terminating reactions involve the interaction of the alkyl and/or trichloromethyl radicals; crystalline hexachloroethane was isolated as a minor by-product in many of the reactions studied.

The result with isobutane is of particular interest in view of the observation[2] that the *t*-butyl radical formed by decomposing bis-trimethylacetyl peroxide (unlike the methyl, *n*-propyl and isopropyl radicals formed from diacetyl, di-*n*-butyryl and diisobutyryl peroxide, respectively) is of insufficient activity to abstract a chlorine atom from carbon tetrachloride. It may be significant that the experiment with the diacyl peroxide was carried out in "warm carbon tetrachloride" while that with isobutane was run at 130–140°.[3]

Experiments with a variety of saturated hydrocarbons and polychloromethanes and -ethanes are summarized in Tables I and II. Good yields of heptyl chlorides, principally a mixture of *s*-heptyl chlorides, were obtained by the conversion of *n*-heptane. Even propane was found to react, a rather good yield of isopropyl chloride being obtained by the reaction of propane with carbon tetrachloride in the presence of di-*t*-butyl peroxide at 138°. On the other hand, no hydrogen–chlorine exchange reaction occurred when ethane was used under similar conditions.

In general, chlorination occurred preferentially at tertiary carbon atoms, probably because of the relative ease of abstraction of a hydrogen atom from a tertiary carbon atom. With bicyclo[2.2.1]heptane, however, the major product was the secondary chloride, 2-chlorobicyclo[2.2.1]-heptane, rather than the bridgehead tertiary chloride, 1-chlorobicyclo[2.2.1]heptane, which may also have been formed.

When hexachloroethane is used as the halogen donor, alkyl chloride is obtained in excellent yield, but the other anticipated product, the pentachloroethane, is not formed. Instead, tetra-

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(1) Presented before the Division of Organic Chemistry at the 116th Meeting of the American Chemical Society, Atlantic City, September, 1949.

(2) A. B. Ash and H. C. Brown, *Record Chem. Progress* (*Kresge-Hooker Sci. Lib.*, **9**, 90 (1948); *cf.* M. S. Kharasch, S. S. Kane and H. C. Brown, THIS JOURNAL, **64**, 1622 (1942).

(3) NOTE ADDED IN PROOF.—On the other hand, the difference in results may be taken as an indication that the acyl peroxide decomposes to yield trimethylacetate radicals rather than *t*-butyl radicals and carbon dioxide; *cf.* F. G. Edwards and F. R. Mayo, *ibid.*, **72**, 1268 (1950).

TABLE I

REACTION OF HYDROCARBONS WITH POLYHALOALKANES

Expt.	Procedure	Reactants, moles Hydrocarbon		RX*n*	Peroxide		Av. temp., °C.	Chief product[a] Formula	B. p., °C.	n^{20}D	Yield %	Ratio[b]
				With carbon tetrachloride								
1	B	i-C_4H_{10}	2.42	0.39	t-Bu_2O_2	0.05	137	Me_2CCl[c]	50–53	1.3950	50	4
2	B	$(Me_2CH)_2$	0.80	.39	t-Bu_2O_2	.04	137	$C_6H_{13}Cl$[d]	112–113	1.4208	57	6
3	B	Me_3CEt	0.52	.49	t-Bu_2O_2	.03	140	$C_6H_{13}Cl$[e]	112–114	1.4225	12	2
4	B	C_3H_8	2.62	.39	t-Bu_2O_2	.05	138	C_3H_7Cl[f]	35–35	1.3790	23	2
5	A	Cyclo-$C_6H_{11}Me$	0.31	.13	Bz_2O_2	.01	92	$C_7H_{13}Cl$[g]	150–154	1.4580	23	3
6	A	C_7H_{12}[h]	1.22	.43	Bz_2O_2	.04	85	$C_7H_{11}Cl$[i]	161–163	1.4845	64	7
				With chloroform								
7	B	n-C_5H_{12}	1.39	.50	t-Bu_2O_2	0.05	137	$C_5H_{11}Cl$	90–100	1.414	12	1
8	B	n-C_7H_{16}	0.80	.42	t-Bu_2O_2	0.03	140	$C_7H_{15}Cl$	152–154	1.423	9	1
				With hexachloroethane								
9	B	i-C_4H_{10}	2.07	.17	t-Bu_2O_2	0.05	138	C_4H_9Cl	50–52	1.3860	106	3
								C_2Cl_4	117–118	1.5010	100	3
10	A	Cyclo-$C_6H_{11}Me$	0.51	.12	Bz_2O_2	0.02	110	$C_7H_{13}Cl$	154–157	1.461	75	4
								C_2Cl_4	119–125	1.490	58	3
				With 1,1,1-trichloroethane								
11	A	n-C_7H_{16}	0.43	.43	Bz_2O_2	0.02	83	$C_7H_{15}Cl$	150–153	1.428	9	2

[a] Other than chloroform or dichloromethane or dichloroethane since no attempt was usually made to isolate these quantitatively. [b] Moles of product per mole of peroxide used. [c] Apparently contaminated with chloroform. [d] Infrared analysis showed 2-chloro-2,3-dimethylbutane to be the major component. [e] Presumably largely 2-chloro-3,3-dimethylbutane. Infrared analysis showed that 1-chloro-3,3-dimethylbutane and 2-chloro-2,3-dimethylbutane were not present in significant quantities. [f] Infrared analysis showed material to be pure isopropyl chloride. [g] Infrared analysis showed 1-chloro-1-methylcyclohexane to be the major component. [h] Bicyclo[2.2.1]heptane; 12 g. of potassium carbonate was also present in the reaction mixture. [i] Infrared analysis indicated that about 90% of the material was 2-chlorobicyclo-[2.2.1]heptane.

TABLE II

REACTION OF *n*-HEPTANE WITH CARBON TETRACHLORIDE

Expt.[a]	Reactants, moles C_7H_{16}	CCl_4	Bz_2O_2	Added subst.	Wt. g.	Temp., °C.	Chloroheptane[b] Moles	%	Ratio[c]
12	0.40	0.39	0.02	....		87	0.087	22	4.4
13	.40	.39	.02	K_2CO_3	14	86	.139	36	7.0
14	.40	.39	.02	Cyclo-C_6H_{10}	5	86	.018	5	0.9
15	.40	.39	.02	$PhNO_2$	6	89	.018	5	0.9
16	.40	1.19	.02	.....		81	.104	26	5.2
17	1.21	0.39	.02	.....		93	.165	42	8.3
18[d]	0.40	.39	.04[e]	.....		137	.160	41	8.0
19	1.21	.39	.02	H_2O	50	93	.225	58	11.2
20	1.26	.40	.02	K_2CO_3	14	89	.242	61	12.1
21	0.40	.39	.02	Cu[f]	10	86	.041	11	2.1
22	.40	.39	.02	Fe[g]	4	86	.089	23	4.5
23	.40	.39	.02	Ag[h]	5	88	.087	22	4.4

[a] Procedure A unless otherwise noted. [b] B. p. 152–156°; n^{20}D 1.423–1.429. [c] Moles of product per mole of peroxide used. [d] Procedure B used. [e] Di-*t*-butyl peroxide. [f] Pellets (1/8"). [g] Wire. [h] Turnings.

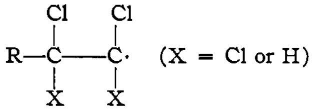
chloroethylene and hydrogen chloride are produced. The mechanism presumably is

$$R\cdot + Cl_3C{-}CCl_3 \longrightarrow RCl + Cl_3C{-}\dot{C}Cl_2 \quad (5)$$

$$Cl_3C{-}\dot{C}Cl_2 \longrightarrow Cl_2C{=}CCl_2 + Cl\cdot \quad (6)$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl \quad (7)$$

This reaction of the pentachloroethyl radical finds analogy in the results obtained in the peroxide-induced reaction of saturated hydrocarbons with polychloroethylenes.[4] In the latter reaction an intermediate radical (I) is formed by the addition of an alkyl radical (derived from the hydrocarbon) to the polychloroethylene



$$R{-}\underset{X}{\overset{Cl}{C}}{-}\underset{X}{\overset{Cl}{\dot{C}}} \quad (X = Cl \text{ or } H)$$

(I)

This radical decomposes to yield a chloroölefin (RCX=CXCl) and a chlorine atom instead of abstracting a hydrogen atom from the hydrocarbon.

The effect of changes in a number of variables is indicated by the results of a series of experiments using *n*-heptane, carbon tetrachloride and benzoyl peroxide (Table II). Increased yields of *s*-heptyl chloride were obtained in the presence of excess *n*-heptane, of water, or of potassium carbonate. The addition of small amounts of cyclohexene, nitrobenzene or copper resulted in markedly decreased yields.

Experimental

Reaction of Hydrocarbons with Chloroalkanes. Procedure A.—A mixture of the hydrocarbon, the polychloroalkane and benzoyl peroxide was heated under reflux for, usually, sixteen hours. The product was washed with dilute alkali to remove benzoic acid, dried with potassium carbonate, and distilled through a 14-inch total reflux fractionation column.[5]

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[4] L. Schmerling and J. P. West, *ibid.*, **71**, 2015 (1949).

[5] C. L. Thomas, H. S. Bloch and J. Hoekstra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 153 (1938).

Procedure B.—The hydrocarbon, the chloroalkane and di-*t*-butyl peroxide were weighed into a glass liner (cooled in a bath at −78° when the gaseous hydrocarbons were employed). The liner was sealed into an Ipatieff-type rotating autoclave of 850-cc. capacity, nitrogen was charged to a pressure of 50 atm., and the autoclave was then heated, the temperature being raised gradually during four hours from 130–140°. The autoclave was permitted to stand overnight, after which the gas was discharged to the atmosphere, and the liquid product was washed, dried and distilled.

Identification of Products.—The chlorinated products were identified by means of their boiling points and refractive indices and in many cases by comparison of their infrared spectra with those of authentic samples (see Table I).

Hexachloroethane was isolated from the higher boiling product of a number of experiments and identified by means of its melting point as well as that of a mixture of the material with an authentic sample of hexachloroethane. Thus, for example, in expt. 13, there was obtained 1.5 cc. of the product boiling at 78–90° at 26 mm. (175–193° at 760 mm.). This became partially crystalline on standing and filtration yielded 0.9 cc. of liquid and 0.8 g. of crystals, which were recrystallized from methanol; m. p. and mixed m. p. 184–185° (sealed tube).

Summary

When a saturated hydrocarbon is treated with certain polyhaloalkanes in the presence of a catalytic amount of a decomposing organic peroxide, hydrogen-halogen exchange occurs and the hydrocarbon is converted to a monohaloalkane. Straight chain paraffins of at least three carbon atoms as well as branched chain and cyclic hydrocarbons may be used.

When hexachloroethane is used as the halogen donor, alkyl chloride is obtained in excellent yield, but the other anticipated product, namely, pentachloroethane, is not formed. Instead, tetrachloroethylene and hydrogen chloride are produced.

RIVERSIDE, ILL. RECEIVED DECEMBER 27, 1949

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE GREAT WESTERN DIVISION, THE DOW CHEMICAL COMPANY]

A New Synthesis of Ethyl Trifluoroacetate

BY T. R. NORTON

Various methods have been described for the preparation of trifluoroacetic acid and the esters thereof. According to the method of Swarts,[1] *m*-aminobenzotrifluoride was oxidized with chromic acid. Chlorinated derivatives of CF_3-$CH{=}CH_2$ have been oxidized with a permanganate and caustic alkali.[2,3] The oxidation of fluorochlorobutenes, such as $CF_3CCl{=}CClCF_3$, with caustic alkali and a permanganate was described by Babcock.[4]

It has been found that trifluoroacetic acid can be prepared in high yield by a less costly and much less drastic type of reaction involving the simple hydrolysis of 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine (III) with dilute aqueous mineral acid at atmospheric pressure.

The method is made practical by an improved synthesis of the previously described compound (III).[5]

Acetonitrile was chlorinated by one of several known methods[6,7] to give trichloroacetonitrile (I).

The trimerization of trichloroacetonitrile was heretofore carried out by contact with anhydrous halogen acids such as hydrogen chloride or hydrogen bromide.[8,9] In contrast to aromatic nitriles, which are readily trimerized,[10] the reaction with trichloroacetonitrile is extremely slow, the time required for completion being on the order of about 100 hours. It has been found that the addition of a small amount of anhydrous aluminum halide to the reaction mixture of trichloroacetonitrile and hydrogen halides greatly activates the latter in causing trimerization of the trichloroacetonitrile, reducing the time required for completion of the reaction to only a few hours and in many cases to less than one hour. The aluminum halides alone are substantially ineffective to cause the trimerization. Their function appears to be solely to serve as an activator for the hydrogen halide. If either (or both) the aluminum halide or hydrogen halide contains bromine as the halide, the reaction rate is increased and pressure is not required as is the case when aluminum chloride and anhydrous hydrogen chloride are used as catalysts. With increasing proportions of aluminum halide the reaction rate increases, although the yield is decreased slightly. The optimum conditions are described in the two examples in the Experimental Section.

The fluorination of 2,4,6-tris-(trichloromethyl)-1,3,5-triazine has been previously described,[5] using anhydrous hydrogen fluoride and a small amount of antimony pentachloride as catalyst. However, the yield of the completely fluorinated product, 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine, was not given but is assumed to be small in view of the drastic conditions employed. It has now been found that the Swarts reaction using antimony

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(1) Swarts, *Bull. Acad. Roy. Belg.*, **8**, 343 (1922).

(2) A. L. Henne, THIS JOURNAL, **67**, 918 (1945).

(3) A. L. Henne, U. S. Patent 2,371,757 (Mar. 20, 1945).

(4) J. H. Babcock and A. D. Kischitz, U. S. Patent 2,414,706 (Jan. 21, 1947).

(5) E. T. McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 391 (1947).

(6) K. Dachlauer, German Patent 694,479 (Aug. 18, 1942).

(7) J. J. Gray and F. Burgess, U. S. Patent 2,426,091 (Aug. 19, 1947).

(8) K. Dachlauer, German Patent 682,391 (Oct. 13, 1939).

(9) K. Dachlauer, German Patent 699,493 (Nov. 30, 1940).

(10) M. A. Kunz, *et al.*, U. S. Patent 1,989,042 (Jan. 22, 1935).