230. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part XV.* Free-radical Chlorination in the Liquid Phase.*

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Alkanes and cycloalkanes can be chlorinated in the liquid phase by reaction with *N*,2,4,6-tetrachloroacetanilide in presence of a small amount of benzoyl peroxide. In this way the relative rates of chlorination of a number of alkanes have been determined by a comparative method. The results support the view that the structure of the hydrocarbon has a marked influence on the rate of chlorination.

N-Chloroamides have been used for some time for the free-radical chlorination of the side chain of alkylbenzenes. There are fewer reports of the halogenation of cycloalkanes by *N*-halogeno-amides; decalin and cyclohexane have been brominated by *N*-bromosuccinimide;[1] cyclohexane, cycloheptane, and decalin have been chlorinated by *N*-chlorosuccinimide;[2] *N*,2,4,6-tetrachloroacetanilide has been used to chlorinate cyclohexane.[3]

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* Part XIV, *J.*, 1961, 2587.

[1] Barnes, *J. Amer. Chem. Soc.*, 1948, **70**, 145; Ford and Waters, *J.*, 1952, 2240.

[2] Buu-Hoï and Demerseman, *J. Org. Chem.*, 1953, **18**, 649.

[3] Ayad, Beard, Garwood, and Hickinbottom, *J.*, 1957, 2981.

There are no reports of the reaction of alkanes with these reagents except for that of Beard[4] who found that 2,2,4-trimethylpentane, when boiled for three weeks with 1% of benzoyl peroxide and *N*,2,4,6-tetrachloroacetanilide, evolved hydrogen chloride and some chlorine.

In this paper it is shown that *N*,2,4,6-tetrachloroacetanilide can be used to chlorinate alkanes.

EXPERIMENTAL

The hydrocarbons used for qualitative chlorination were the purest available; before use, they were distilled from sodium after passage through a column of active silica gel.

Chlorinations.—The following standard method was used for the qualitative chlorination of saturated hydrocarbons. *N*,2,4,6-Tetrachloroacetanilide (0·074 mole), benzoyl peroxide (0·009 mole), and an excess of the hydrocarbon were stirred together at 90° (thermostat) under a condenser. After about 5 min. the solution began to darken, and it had become brownish-red after 30—60 min., the flask being filled with needle-like crystals. After all the chloramine had reacted the mixture was poured into light petroleum (b. p. <40°) (250 c.c.), and the precipitate (A) was collected and washed with light petroleum (b. p. <40°) (150 c.c.). The combined filtrate and washings were freed from solvent, and the residue of chlorinated products was fractionated.

The precipitate (A) (15—16·8 g.) was 2,4,6-trichloroacetanilide, m. p. 205—206·5° (from ethanol).

Chlorination produced essentially a mixture of monochloroalkanes, which could not be resolved into its components. By gas–liquid chromatography, the proportion of primary chloro-compound in the product could be estimated; only a partial separation of some of the secondary chloro-compounds was achieved by this means.

(i) n-Heptane, b. p. 99·5°, n_D^{20} 1·3876, gave chloroheptanes, b. p. 50—58°/24 mm., n_D^{20} 1·4288—1·4236 (40%) (Found: C, 62·7; H, 10·6; Cl, 26·3. Calc. for $C_7H_{15}Cl$: C, 62·5; H, 11·1; Cl, 26·3%). By gas-liquid chromatography it was estimated that the product contained 12·3% of 1-chloroheptane.

(ii) n-Decane, b. p. 82°/34 mm., n_D^{20} 1·4121, gave after 1 hr. a 50% yield of chlorodecanes, b. p. 102—108°/22 mm., n_D^{20} 1·4372—1·4388 (Found: C, 68·5; H, 11·8; Cl, 19·7. Calc. for $C_{10}H_{21}Cl$: C, 68·0; H, 12·0; Cl, 20·1%), containing 10·2% of 1-chlorodecane. Asinger *et al.*[5] found that photochlorination at 60° gave a monochlorinated product containing 11·6% of 1-chlorodecane.

(iii) n-Dodecane b. p. 114°/27 mm., n_D^{20} 1·4216, after 5 hr. gave a 32% yield of chlorododecanes, b. p. 52·5—54°/0·15 mm. (Found: C, 71·3; H, 12·2; Cl, 16·7. Calc. for $C_{12}H_{25}Cl$: C, 70·4; H, 12·3; Cl, 17·3%).

(iv) n-Octadecane, m. p. 28·5°, b. p. 153°/3 mm., after 45 hr. gave a mixture of mono- and di-chloro-octadecanes, b. p. 119—148°/0·15 mm., n_D^{20} 1·4475—1·4647. The chlorine content for various fractions from distillation ranged between 9% and 23% and no satisfactory separation was achieved.

(v) 2,2,4-Trimethylpentane, b. p. 100°, n_D^{20} 1·3915, after 18 hr. gave a mixture of chloro-2,2,4-trimethylpentanes, b. p. 54—55°/20 mm., n_D^{20} 1·4328 (50%) (Found: C, 64·8; H, 11·9; Cl, 23·3. Calc. for $C_8H_{17}Cl$: C, 64·7; H, 11·5; Cl, 23·9%).

(vi) 2,3,4-Trimethylpentane, b. p. 113·5°, n_D^{20} 1·4042, was not completely chlorinated after 24 hr.; the product, b. p. 65—70°/15 mm., n_D^{20} 1·4403 (29%), was monochloro-2,3,4-trimethylpentane (Found: C, 65·7; H, 11·7; Cl, 22·3. Calc. for $C_8H_{17}Cl$: C, 64·7; H, 11·5; Cl, 23·9%).

(vii) Methylcyclohexane, b. p. 100°, n_D^{20} 1·4237, gave after 3 hr. chloro(methylcyclohexanes), b. p. 58—65°/19 mm., n_D^{20} 1·4595—1·4603 (Found: C, 64·1; H, 9·8; Cl, 26·2. Calc. for $C_7H_{13}Cl$; C, 63·4; H, 9·9; Cl, 26·7%).

(viii) Decahydronaphthalene was a mixture of *cis*- and *trans*-isomers, b. p. 187—192°, n_D^{20} 1·4767. The usual amount of benzoyl peroxide as a promoter in these chlorinations caused formation of much tar and copious evolution of hydrogen chloride with only a poor yield of chlorinated product. By using a smaller amount of peroxide (0·05 g. instead of 2·2 g.) the yield of chlorodecahydronaphthalenes, b. p. 103—110°/15 mm., n_D^{20} 1·4960—1·4993, was 37% (Found, for successive fractions: C, 70·1, 70·0, 69·9; H, 10·1, 10·1, 9·9; Cl, 20·1, 20·1, 20·0. Calc. for $C_{10}H_{17}Cl$: C, 69·6; H, 9·9; Cl, 20·5%).

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[4] Beard, Thesis, London, 1958.

[5] Asinger, Geisler, and Schmiedel, *Chem. Ber.*, 1959, **92**, 3085.

Relative Rates of Chlorination.—The n-alkanes were purified through their urea complexes, then passed through active silica gel and distilled from sodium through efficient columns.

The isoalkanes were all pure samples. They were passed through active silica gel and distilled from sodium.

The course of the chlorination of alkanes by *N*,2,4,6-tetrachloroacetanilide under the influence of benzoyl peroxide is essentially the same as of other free-radical chlorinations and is represented by $R\cdot + TCl \longrightarrow RCl + T\cdot$; $T\cdot + AlkH \longrightarrow TH + Alk\cdot$; $Alk\cdot + TCl \longrightarrow AlkCl + T\cdot$; where $R\cdot$ is a free radical from benzoyl peroxide and TCl = *N*,2,4,6-tetrachloroacetanilide.

Estimation of the rate of chlorination is based on a comparison of the rate of disappearance of the active chlorine of *N*,2,4,6-tetrachloroacetanilide in a standard alkane, usually n-heptane, with that in the hydrocarbon under examination. The accuracy of the method depends on the absence of side reactions which interfere with the course given above or consume chlorine. One such reaction is the decomposition of *N*,2,4,6-tetrachloroacetanilide under the influence of benzoyl peroxide to give 2,4,6-trichloroacetanilide, the chloroacetyl derivative of 2,4,6-trichloroaniline, and other products. This occurs also with other organic compounds containing active chlorine, such as alkyl hypochlorites,[6] *N*-chloro-sulphonamides,[7] and *N*-halogeno-alkylamines.[8] Conditions for quantitative chlorination of the alkanes were selected to prevent this side reaction; the purity of the trichloroacetanilide from each chlorination is evidence that it did not occur here to any appreciable extent. The same test also established that dimerisation of the trichloroacetanilide radical was not sufficiently important to influence the reaction. Interference in the course of chlorination may also result from (*a*) dismutation of the alkyl free radical, (*b*) breakdown of the alkyl radical to lower products, or (*c*) dimerisation of the alkyl radical. Evidence that (*a*) and (*b*) are not important is provided by the absence of appreciable amounts of olefin from the products of chlorination. Precautions were also taken to ensure a uniform solution of the *N*-chloro-compound, since it was found that dichlorination occurred unless this was strictly observed. Indeed it appears that side reactions have no serious influence until at least 60% of the *N*-chloro-compound is consumed; thereafter, deviations occur from the straight line representing the relation between time and the disappearance of *N*-chloro-compound.

Measurement of Chlorination Rate.—Preliminary experiments established that the rate of chlorination is markedly influenced by air and consequently all measurements were made on hydrocarbons which had been deoxygenated by refluxing them in a stream of nitrogen.

Consistent and reliable results were obtained by comparing, under the same conditions, the rate of disappearance of *N*,2,4,6-tetrachloroacetanilide in a hydrocarbon with that in a standard hydrocarbon, usually n-heptane. For this purpose M/100-solutions of *N*,2,4,6-tetrachloroacetanilide in the appropriate hydrocarbons were used, each solution containing M/1000-benzoyl peroxide. Equal portions of these solutions were measured into ampoules covered with tin foil. All these operations were carried out in an air-tight dry-box filled with nitrogen. The ampoules were then sealed and immersed in a thermostat bath at 85° ± 0·2°. They were removed at intervals and the unchanged *N*-chloro-compound was estimated iodometrically. The results, measured from a plot of the percentage of *N*-chloro-compound which has reacted against time, can be expressed as a straight line until the concentration of *N*-chloro-compound has fallen to about 60—80% of its original value. The rate of the reaction is independent of time and is represented by the slope of the curve. The results are recorded in Tables 1—3.

TABLE 1.

Relative reactivity of n-alkanes towards *N*,2,4,6-trichloroacetanilide at 85°.

	C_6	C_7	C_8	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}
Calc. ……………	0·83	1	1·17	1·54	1·73	1·88	2·25	2·58	2·93	3·45
Obs. ………………	0·96	1	1·12	1·36	1·53	1·64	1·76	1·95	2·22	2·25

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[6] Greene, Savitz, Lau, Osterholz, and Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 2196; Walling and Padwa, *ibid.*, p. 2207.

[7] Fuller, personal communication.

[8] Löffler *et al.*, *Ber.*, 1909, **42**, 3427, 3421; 1910, **43**, 2025; Wawzonek *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 2118; 1951, **73**, 2806; 1959, **81**, 3367; Corey and Hertler, *ibid.*, 1960, **82**, 1657.

TABLE 2.

Reactivities of isoalkanes towards *N*,2,4,6-tetrachloroacetanilide, relative to n-heptane = 1·0, at 85°.

A = 2-methylheptane.
B = 3-methylheptane.
C = 2,2,4-trimethylpentane.
D = 2,3,3-trimethylpentane.
E = 2,3,4- ,,
F = 2,2,5-trimethylhexane.
G = 2,6-dimethyloctane.
H = 2,2,4,4,6-pentamethylheptane.
I = 2,2,4,6,6-pentamethylheptane.

	A	B	C	D	E	F	G	H	I
Obs.	1·50	1·61	0·29	1·20	2·33	0·98	2·55	1·07	0·82
Calc.	1·61	[1·61]	1·21	1·21	2·52	1·38	2·40	1·50	1·50

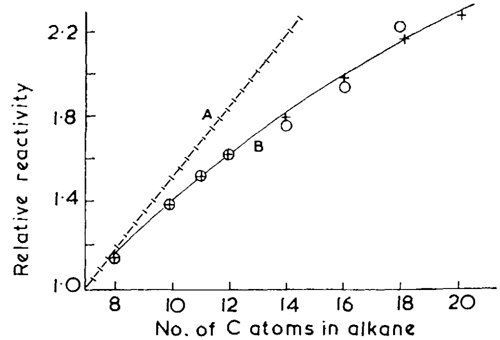
TABLE 3.

Reactivities of cycloalkanes, relative to n-heptane = 1, towards *N*,2,4,6-tetrachloroacetanilide at 85°.

	Cyclohexane	Methylcyclohexane	Ethylcyclohexane
Obs.	1·66	3·32	4·22
Calc.	1·06	1·67	1·85

DISCUSSION

If the relative reactivities of the primary and secondary hydrogen atoms of a n-alkane towards chlorination are constant throughout the homologous series, the overall rate of chlorination of any member of the series can be calculated from the expression, $K(n_{\mathrm{p}} + Rn_{\mathrm{s}})$,



(A) Reactivity of n-alkanes towards *N*,2,4,6-tetrachloroacetanilide, relative to n-heptane (=1), calculated from the expression $(n_{\mathrm{p}} + 4{\cdot}3n_{\mathrm{s}})$. (B) Reactivity calculated from the expression $2(n_{\mathrm{p}} + 4{\cdot}3n_{\mathrm{s}})/(N + 46)$: (○) observed and (+) calculated values.

where R = relative reactivity of secondary hydrogen with respect to the primary, and n_{p} and n_{s} are the number of primary and secondary hydrogen atoms, respectively, in the hydrocarbon. This expression was applied by Chambers and Ubbelohde [9] to the lower alkanes. Its extension to the higher members is less satisfactory. The calculated values differ from the observed values and the divergence increases with increasing molecular weight. It may be inferred that the original assumption that the relative reactivity of primary and secondary hydrogens in a n-alkane are constant throughout the homologous series (see Figure) is not justified. Substantial agreement with the observed values can be obtained using the empirical expression: $k(n_{\mathrm{p}} + Rn_{\mathrm{s}})/(k' + N)$, where N = total number of hydrogen atoms in the hydrocarbon, $k = 2$, $k' = 46$, and $R = 4{\cdot}3$. The value 4·3 for the relative sensitivity of a secondary hydrogen atom of a n-alkane is derived from estimation of the proportions of primary and secondary heptyl chlorides formed in the chlorination of n-heptane. Asinger *et al.*[5,10] report a ratio of about 1 : 3 derived from the

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[9] Chambers and Ubbelohde, *J.*, 1955, 285.

[10] Asinger, *Ber.*, 1942, **75**, 670.

photochlorination of n-decane, n-hexadecane, and n-octadecane. Hass *et al.*[11] calculated the ratios primary : secondary : tertiary to be 1 : 3·25 : 4·4 at 27° from the chlorination of the lower alkanes. Anson *et al.*[12] report ratios of 1 : 3·9 : 5·1.

No direct determination has been made of the relative susceptibility of the tertiary hydrogen atoms of isoalkanes to replacement by chlorine by reaction with *N*,2,4,6-tetrachloroacetanilide. An approximate value has been calculated from the rate of 3-methylheptane relative to that of n-heptane; this is known accurately from a number of concordant estimations to be 1·61. From it the relative susceptibility of primary to tertiary is 1 : 37, a ratio which reflects the selectivity of *N*,2,4,6-tetrachloroacetanilide as a chlorinating agent.

For branched-chain alkanes there is clear evidence that the relative reactivities of the primary, secondary, and tertiary hydrogen towards substitution are not the only factors to determine the rate of substitution. Thus 2,2,4-trimethylpentane is chlorinated much more slowly than its isomer (Table 2), 2,2,3-trimethylpentane, although it might be expected that they should react at the same rate. Brook[13] noted that 2,2,4-trimethylpentane is much less reactive towards t-butoxy-radicals than might be expected. Foster and Hickinbottom[14] made a similar observation about its relative inertness to oxidation by chromic acid.

Brook[13] suggested that the tertiary hydrogen in 2,2,4-trimethylpentane is shielded from attack by the t-butoxy-radical by the configuration of the molecule. A similar explanation may be applied to chlorination with *N*,2,4,6-tetrachloroacetanilide, the tertiary hydrogen being almost completely shielded. This view, that configuration of the molecule is an important factor in determining the rate of chlorination, is supported by our results with 2,2,4,4,6- and 2,2,4,6,6-pentamethylheptanes.

The rates of chlorination of the cycloalkanes are of special interest in that the difference between the calculated and the observed rates suggests that factors other than those discussed above are concerned. Brook also found that secondary and tertiary hydrogen atoms of the cycloalkanes and their alkyl derivatives are approximately 1½ times as reactive towards t-butoxy-radicals as are those in the alkanes.

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[11] Hass, McBee, and Weber, *Ind. Eng. Chem.*, 1936, **28**, 333.
[12] Anson, Fredericks, and Tedder, *J.*, 1959, 918.
[13] Brook, *Trans. Faraday Soc.*, 1957, **53**, 327.
[14] Foster and Hickinbottom, *J.*, 1960, 680.