Preparative scale gas chromatography on a 6-ft. Apiezon preparative column afforded sufficient quantities of the two main fractions for characterization.

The largest of the two main fractions had the smallest retention volume. Its infrared spectrum showed a typical *ortho*-disubstitution pattern between 5 and 6 $\mu$ and was, therefore, identified as *o*-nitrophenylcyclopropane. This substance is an oil ($n^{20}\text{D}$ 1.5606) which could not be made to crystallize; $\lambda_{\text{max.}}^{\text{C}_2\text{H}_5\text{OH}}$ 211, 249 m$\mu$; $\epsilon$ 1150; 4550. The smaller of the two main fractions, having the larger retention volume, showed an absorption pattern in the 5–6-$\mu$ region typical of *p*-disubstituted benzenes and was identified as *p*-nitrophenylcyclopropane. This isomer is a low melting solid, m.p. 32–33°; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 218, 280 m$\mu$ ($\epsilon$ 8080, 11,000).

*Anal.* Calcd. for $C_9H_{10}NO_2$: C, 66.24; H, 5.56; N, 8.58. Found for *o*-nitrophenylcyclopropane: C, 65.98; H, 5.40; N, 8.54. Found for *p*-nitrophenylcyclopropane: C, 66.25; H, 5.54; N, 8.67.

**Oxidation of *o*-Nitrophenylcyclopropane.**—A sample of 0.50 g. (3.1 mmoles) of *o*-nitrophenylcyclopropane was heated under reflux for 2 hr. with a solution of 4.3 g. (43 mmoles) of chromic acid, 5.7 ml. of concentrated sulfuric acid, and 8.5 ml. of water. The reaction mixture was diluted with water and extracted with ether. The extract was dried and concentrated to give the crude product which on crystallization gave 0.33 g. (64%), m.p. 140–144° (lit.[14] m.p. 147–147.5°), of *o*-nitrobenzoic acid, identical with an authentic sample (mixture melting point and infrared spectrum).

**Oxidation of *p*-Nitrophenylcyclopropane.**—A sample of 100 mg. (0.61 mmole) of *p*-nitrophenylcyclopropane was heated under reflux for 2 hr. with a solution of 0.85 g. (8.5 mmoles) of chromic acid and 1.1 ml. of concentrated sulfuric acid in 2 ml. of water. The reaction mixture was diluted with water and the solid was collected to afford 90 mg. (88%) of *p*-nitrobenzoic acid, m.p. 240–242° (lit.[14] m.p. 239–240°), identical with an authentic sample (infrared spectra and mixture melting point).

**Nitrations of Alkylbenzenes and Analysis of the Product Mixtures.**—To a solution of 26.1 g. (24 ml., 0.26 mole) of acetic anhydride and 10.9 g. (7.3 ml., 0.16 mole) of fuming nitric acid (density 1.49–1.50) at −50° was added dropwise with stirring 0.05 mole of the alkylbenzene. The reaction mixture was allowed to come to room temperature (30 min.) and was poured into hot water. The product mixture was extracted with ether, the extract was dried, and concentrated to give the crude residue (always above 95% of the theoretical amount). This was dissolved in acetone in a 25-ml. volumetric flask and analyzed on a 10-ft. silicone rubber, analytical column (Aerograph A-90-C equipped with a disk integrator). The ratio of the areas under the two peaks was taken as the *ortho–para* ratio. Each analysis was carried out at least three times; the analyses were reproducible within ±1%. The total yields based on the gas chromatograms were always above 90%. These values are subject to errors of ±3%, owing to variations in the sample size. The gas chromatograms gave evidence for only very small amounts of unchanged starting materials, *meta* isomers, and polynitro compounds.

A second series of nitrations with acetic anhydride–fuming nitric acid prepared at room temperature was carried out in the same manner. Here also the yields were above 90%. In this case, nitration of phenylcyclopropane produced a rather wide range of *ortho–para* ratios.

**Nitration of Phenylcyclopropane with Nitric Acid–Sulfuric Acid.**—A sample of 2.3 g. of phenylcyclopropane was nitrated in 3.83 g. sulfuric acid and 1.42 g. of nitric acid according to the method of Brown and Bonner.[4] The crude yield was 2.30 g. (78%). The chromatographic analysis is given in Table I.

**Infrared and Ultraviolet Spectra.**—Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were recorded in 95% ethanol on a Carey Model 11 ultraviolet spectrophotometer.

**Acknowledgment.**—The authors wish to thank Dr. L. A. Strait for many helpful discussions and Mr. Michael Hrenoff for determining some of the infrared and ultraviolet spectra.

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# Competition Reactions of Cycloalkanes with Trichloromethanesulfonyl Chloride and Bromotrichloromethane

EARL S. HUYSER, HAROLD SCHIMKE,[1a]
AND ROBERT L. BURHAM[1b]

*Department of Chemistry, University of Kansas,*
*Lawrence, Kansas*

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The suggestion was made in an earlier publication that the hydrogen abstracting radical in the peroxide- and light-induced chlorinations of hydrocarbons with trichloromethanesulfonyl chloride (I) was not the trichloromethyl radical.[2] This conclusion was based on the difference in the relative reactivities of toluene and cyclohexane toward chlorination by I and toward bromination by bromotrichloromethane. Two different free radical chain sequences were suggested to account for the products obtained from the reaction of trichloromethanesulfonyl chloride with hydrocarbons (equation 1).

$$\underset{\text{I}}{\text{Cl}_3\text{CSO}_2\text{Cl}} + \text{RH} \longrightarrow \text{RCl} + \text{SO}_2 + \text{HCCl}_3 \tag{1}$$

CHAIN SEQUENCE A

$$\text{R}\cdot + \text{Cl}_3\text{CSO}_2\text{Cl} \longrightarrow \text{RCl} + \text{Cl}_3\text{C}\cdot + \text{SO}_2 \tag{2}$$

$$\text{Cl}_3\text{C}\cdot + \text{RH} \longrightarrow \text{HCCl}_3 + \text{SO}_2 \tag{3}$$

CHAIN SEQUENCE B

$$\text{R}\cdot + \text{Cl}_3\text{CSO}_2\text{Cl} \longrightarrow \text{RCl} + \text{Cl}_3\text{CSO}_2\cdot \tag{4}$$

$$\text{Cl}_3\text{CSO}_2\cdot + \text{RH} \longrightarrow \text{Cl}_3\text{CSO}_2\text{H} + \text{R}\cdot \tag{5}$$

$$\text{Cl}_3\text{CSO}_2\text{H} \longrightarrow \text{HCCl}_3 + \text{SO}_2 \tag{6}$$

In Chain Sequence A, the hydrogen abstraction from the hydrocarbon is performed by the trichloromethyl radical (equation 2) whereas in Chain Sequence B, the trichloro methanesulfinyl radical ($\text{Cl}_3\text{CSO}_2\cdot$) is postulated to be the hydrogen abstracting radical (equation 5). The trichloromethanesulfinic acid formed in this reaction is reported to be unstable, decomposing into chloroform and sulfur dioxide.[3] The peroxide- and light-induced brominations of hydrocarbons by bromotrichloromethane (equation 7) very likely involve the

$$\text{BrCCl}_3 + \text{RH} \longrightarrow \text{RBr} + \text{HCCl}_3 \tag{7}$$

free radical chain sequence (8 and 9), a sequence which almost certainly involves hydrogen abstraction

$$\text{R}\cdot + \text{BrCCl}_3 \longrightarrow \text{RBr} + \text{Cl}_3\text{C}\cdot \tag{8}$$

$$\text{Cl}_3\text{C}\cdot + \text{RH} \longrightarrow \text{HCCl}_3 + \text{R}\cdot \tag{9}$$

by a trichloromethyl radical.[4] A comparison of the relative reactivities of the medium-size cycloalkanes toward halogenation by trichloromethanesulfonyl chloride

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[1] (a) Pacific University, Forest Grove, Ore., National Science Foundation Research Participant, Summer, 1961; (b) Grand View College, Des Moines, Iowa, National Science Foundation Research Participant, Summer, 1962.

[2] E. S. Huyser and B. Giddings, *J. Org. Chem.*, **27**, 3391 (1962); E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 5246 (1960).

[3] M. Battegay and W. Kern, *Bull. soc. chim.*, **41**, 38 (1927).

[4] E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960); E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); see also G. A. Russell, C. DeBoer, and K. M. Desmond, *J. Am. Chem. Soc.*, **85**, 365 (1963).

and by bromotrichloromethane support the suggestion made previously that Chain Sequence B is operative in the chlorinations of hydrocarbons with trichloromethanesulfonyl chloride.

The relative reactivities of cyclopentane, cyclohexane, cycloheptane, and cyclooctane toward reaction with trichloromethanesulfonyl chloride and bromotrichloromethane are shown in Table 1. These values were determined by competition reactions (see Experimental) of the cycloalkanes toward halogenation by the indicated reagent. That the same radical is not involved in the hydrogen abstraction in the two cases is evident from the different relative reactivities of these cycloalkanes toward halogenation by trichloromethanesulfonyl chloride and bromotrichloromethane. Cyclopentane and cyclohexane have essentially the same reactivity toward reaction with trichloromethanesulfonyl chloride, whereas cyclopentane is more reactive than cyclohexane in reaction with bromotrichloromethane. Although the relative reactivity of cycloheptane with respect to cyclohexane is very nearly the same toward both trichloromethanesulfonyl chloride and bromotrichloromethane, cyclooctane is at least two times more reactive than cycloheptane toward the latter reagent.

TABLE I

RELATIVE REACTIVITIES OF CYCLOALKANES TOWARD REACTION WITH TRICHLOROMETHANESULFONYL CHLORIDE AND BROMOTRICHLOROMETHANE AT 80°

| Cycloalkane | Relative reactivity[a] | No. of runs |
|---|---|---|
| | $Cl_3CSO_2Cl$ | |
| Cyclopentane | 1.00[b] ± 0.07 | 14 |
| Cyclohexane | 1.00 | .. |
| Cycloheptane | 2.67 ± 0.16 | 4 |
| Cyclooctane | 4.20[c] ± 0.04 | 3 |
| | $BrCCl_3$ | |
| Cyclopentane | 1.57 ± 0.17 | 18 |
| Cyclohexane | 1.00 | .. |
| Cycloheptane | 3.30 ± 0.50 | 10 |
| Cyclooctane | 9.20[d] ± 0.54 | 7 |

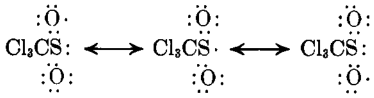
[a] Relative to a unit reactivity of cyclohexane. [b] Average deviation from average value obtained from number of runs indicated. [c] Determined from relative reactivity of cyclooctane with respect to cycloheptane which was 1.57 ± 0.02. [d] Determined from relative reactivity of cyclooctane with respect to cycloheptane which was 2.79 ± 0.18.

Two factors are probably responsible for the difference in the reactivities of the cycloalkanes toward hydrogen abstraction. These are (1) the relative stabilities of the cycloalkyl radicals that are produced, and (2) the relative stabilities of the cycloalkyl carbonium ions, a factor arising from polar contributions encountered in the transition state of the hydrogen abstraction reactions. Both of these factors may be important if there is a considerable amount of bond breaking in the transition state of the reaction as shown for hydrogen abstraction by the trichloromethyl radical.

$$\overset{\delta^+}{[\mathrm{R}}\ldots\mathrm{H}\ldots\ldots\overset{\delta^-}{\mathrm{CCl_3}]}$$

The inferred order of stability of the cycloalkyl radicals and carbonium ions based on kinetic measurements involving other systems[5] and, consequently, the predicted order of reactivity of the cycloalkanes toward hydrogen abstraction is cyclooctyl > cycloheptyl > cyclopentyl > cyclohexyl. The observed orders of reactivity of the cycloalkanes toward reaction with both trichloromethanesulfonyl chloride and bromotrichloromethane are consistent with this prediction.

The lower degree of specificity found for the reactions with trichloromethanesulfonyl chloride suggests that the extent of bond breaking in the hydrogen abstraction step in the reactions of this reagent is less than that in hydrogen abstractions by the trichloromethyl radical. A lower degree of bond breaking compared to that encountered in the hydrogen abstractions by the trichloromethyl radical might well be expected if the $Cl_3CSO_2\cdot$ were the hydrogen abstractor (Chain Sequence B). The dissociation energy ($D_{\mathrm{C-H}}$) for the carbon–hydrogen bond in the cycloalkanes is ~94 kcal./mole.[6] Hydrogen abstraction by a trichloromethyl radical is a process which is endothermic to the extent of ~5 kcal./mole ($D_{\mathrm{Cl_3C-H}}$ 90 kcal./mole[6]). The bond dissociation energy of an oxygen–hydrogen bond in $(CH_3)_3CO{-}H$ is ~104 kcal./mole,[7] and, although resonance stabilization of the trichloromethanesulfinyl radical might be expected to lower the oxygen–hydrogen bond dissociation



$$\mathrm{Cl_3C}\overset{:\ddot{O}\cdot}{\underset{:\ddot{O}:}{\ddot{S}}}: \longleftrightarrow \mathrm{Cl_3C}\overset{:\ddot{O}:}{\underset{:\ddot{O}:}{\ddot{S}}}\cdot \longleftrightarrow \mathrm{Cl_3C}\overset{:\ddot{O}:}{\underset{:\ddot{O}\cdot}{\ddot{S}}}:$$

energy in trichloromethanesulfinic acid to some extent, it does not seem unlikely that $D_{\mathrm{Cl_3C\overset{O}{S}O-H}}$ may be above 94 kcal./mole. This would make hydrogen abstraction from a cycloalkane by $Cl_3CSO_2\cdot$ an exothermic reaction. Such a reaction, in terms of the Hammond postulate,[8] might be expected to involve a transition state with less bond breaking than encountered in the endothermic hydrogen abstraction by $Cl_3C\cdot$. Contribution to the transition state involving stabilities of the cycloalkyl radical and carbonium ions would not be so great and, hence, the differences in reactivity less pronounced.

Although apparently less selective as a halogenating agent that bromotrichloromethane, trichloromethanesulfonyl chloride is a far more selective chlorinating agent than chlorine itself. The ratio of reactivities of $C_8H_{16}$:$C_7H_{14}$:$C_5H_{10}$:$C_6H_{12}$ toward chlorination with chlorine was found by Russell[9] to be 1.5:1.0:1.0:1.0 at 40°. In 12 *M* carbon disulfide, a solvent which markedly enhances the selectivity of chlorine atoms as hydrogen abstractors, the ratio of reactivities was found to be 3.8:2.0:1.2:1.0 at 40° for $C_8H_{16}$:$C_7H_{14}$:$C_5H_{10}$:$C_6H_{12}$,[9] a degree of selectivity somewhat less than we observed in reactions with trichloromethanesulfonyl chloride at 80°.

### Experimental

The nature of the products and the stoichiometry of the reactions of trichloromethanesulfonyl chloride and bromotrichloromethane with hydrocarbons are discussed in earlier reports (see ref. 2 and 3).

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(5) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951); C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *ibid.*, **75**, 2078 (1953).

(6) *Cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chap. 2, for tables of bond dissociation energies and discussion of their use in free radical reactions.

(7) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(8) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(9) G. A. Russell, *ibid.*, **80**, 4997 (1958).

The relative reactivities shown in Table I were determined by competition reactions performed in the following manner. A mixture consisting of known amounts of two of the cycloalkanes was allowed to react with about a half of an equivalent amount of the halogenating agent. Benzene or chlorobenzene also was added in an amount equivalent to the cycloalkanes to serve as an internal standard for the gas chromatographic analysis. The reactions were performed in sealed tubes, induced with benzoyl peroxide, and allowed to proceed at the indicated temperature until about 30–70% of the halogenating reagent had been consumed. Relative reactivity ratios, that is the ratio of the reaction rate constants of the particular cycloalkanes toward attack by the hydrogen abstracting radical, were calculated in the usual manner using the equation, $\frac{k_A}{k_B} = \log (A_{\text{init}}/A_{\text{fin}})/\log (B_{\text{init}}/B_{\text{fin}})$, where the subscript, init and fin refer to the amounts of the cycloalkanes A and B before and after the reaction, respectively. The value for the amounts of the two cycloalkanes remaining after reaction were obtained by gas chromatographic analysis of the reaction mixtures.

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## Solubilities of Organic Salts in Hydrocarbons[1]

N. C. DENO AND HENRY E. BERKHEIMER

*Pennsylvania State University, University Park, Pennsylvania*

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It is known generally that salts of large organic ions are more soluble in organic solvents than salts of small inorganic ions. It might be imagined that this is a result of some specific attractive forces between organic molecules. However, solubilities of a wide variety of hydrocarbons in water[2,3] have been correlated by an equation whose derivation specifically assumed that energies arising from van der Waals or London forces were the same for hydrocarbon–hydrocarbon interactions as for hydrocarbon–water attractive forces.

This cancelling out of energies arising from London dispersion forces can be rationalized this way. Let us consider a molecule such as benzene immersed first in water and then in hexane. The energy arising from London forces between two small spherical molecules in the gas phase is given by this well known equation.

$$E = (-3/2)(\alpha_1\alpha_2/r^6)I_1I_2/(I_1 + I_2) \qquad (1)^4$$

The polarizability, $\alpha$, and ionization potential, $I$, for benzene are common factors for equation 1 applied to either benzene–water or benzene–hexane. The ionization potentials for water and hexane are 12.5 and 10.5 e.v.[5] Although the absolute difference between these two numbers may seem large, the per cent difference is small when used in equation 1 so that only small energy differences arise from differences in ionization potential. The relative invariance of ionization potential is characteristic of compounds of C, H, O, and N, and these are of primary interest in organic chemistry. When elements such as sulfur, iodine, etc., are introduced, their effect is overshadowed by the mass of hydrocarbon so that, on the average, the effective ionization potential for intermolecular attractions is that of a typical hydrocarbon.

The electronic polarizabilities of water and hexane are 3.70 and 29.8 cm.$^3$/mole.[6] These values initially seem much different, but what governs interaction energies in solution is the polarizability per unit volume of the solvents. These values are 0.21 and 0.23 for water and hexane, respectively. The London dispersion forces will nearly cancel, and this result can be generalized to most systems of interest in organic chemistry.

Table I presents data on the solubilities of a series of $R_4NClO_4$ salts. It is evident that the solubility in benzene (or ethanol) relative to water increases as the size of R increases. Such results cannot be rationalized by a consideration of ion–solvent electrostatic forces. Such forces must always be greater in water than benzene leading to the erroneous expectation that the salts will always be more soluble in water. Neither can such results be rationalized by a consideration of London forces since the energies arising from such forces cancel, as explained in the preceding paragraph. It is evident that any explanation based only on solute–solvent interaction energies fails.

TABLE I

RELATIVE SOLUBILITIES OF $R_4N^+$ SALTS (25°)[a]

| | —Solubility in moles/l.— | | | —Relative solubility— | |
|---|---|---|---|---|---|
| Salt | Water | Ethanol | Benzene | EtOH-$H_2O$ | $C_6H_6$–$H_2O$ |
| $KClO_4$[b] | 0.149 | 0.00065 | | 0.0044 | |
| $RbClO_4$[b] | .071 | .00039 | | .0055 | |
| $CsClO_4$[b] | .085 | .00037 | | .0044 | |
| $(CH_3)_4NClO_4$ | .075 | .00089 | 0.000165 | .0119 | 0.0022 |
| $(C_2H_5)_4NClO_4$ | .217 | .0114 | .000113 | .0525 | .00052 |
| $(C_3H_7)_4NClO_4$ | .0204 | .0149 | .000075 | .75 | .0037 |
| $(C_6H_5)_4NClO_4$ | .000187 | .00102 | .000176 | 5.45 | .94 |
| $(C_5H_{11})_4NClO_4$ | .00067 | .037 | .00111 | 56 | 1.67 |
| $(C_6H_{13})_4NClO_4$ | .00044 | .292 | .871 | 660 | 2000 |
| $(CH_3)_4NI$[b] | 0.26 | 0.0045 | | 0.017 | |
| $(C_2H_5)_4NI$[b] | 1.4 | .38 | | .27 | |
| $(C_3H_7)_4NI$[b] | 0.60 | .64 | | 1.1 | |

[a] The solid phase in equilibrium with the saturated ethanol solution was analyzed in each case and shown to be the simple $R_4NClO_4$ salt (Table II). Data on $(C_4H_9)_4NClO_4$ is omitted because Ralph Seward of Pennsylvania State University found that the phase in equilibrium with the saturated solution in benzene contained benzene in the crystal lattice. The alkyl groups are the straight chain *n*-alkyl groups except for $C_6H_5$, which is phenyl. [b] Data from A. Seidell, "Solubilities," D. Van Nostrand Co., New York, N. Y., 1960.

The answer lies in solvent–solvent forces and the principle of volume energies.[2,3,7,8] Briefly, it costs energy to make a hole in the solvent to place a solute molecule or ion. This energy is the product of the volume of the hole times the internal pressure of solvent. This energy will be greater for a solvent such as water with its high internal pressure arising from intermolecular hydrogen bonding. In contrast, this energy will be much smaller for most organic liquids in which the intermolecular forces are predominantly London forces.[4] In the series listed in Table I, as the size of R increases,

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[1] This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

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[6] Calculated by the familiar relation, $(n^2 - 1)(n^2 - 2)/(M/e)$.

[7] F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

[8] H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.*, **32**, 119 (1960); F. H. Stillinger, Jr., "Equilibrium Theory of Pure Fused Salts," a chapter in "Selected Topics in the Physical Chemistry of Molten Salts," Milton Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.