the weight average molecular weight must be used in viscosity studies on inhomogeneous polymers (like those used technically) as prescribed by Kraemer and Lansing.

The Staudinger viscosity constant K is strongly molecular weight dependent, especially at low molecular weights while K_w from the equation (1) containing an additive constant B is satisfactorily independent at least down to $M_w = 5000$. Hence K_w for large molecules appears to contain no factors dependent on chain length.

The additive constant B has similar values for several linear polymer series containing flexible chains, providing the chain length exceeds some minimum. It possibly reflects a statistical property of chain kinking needed to relate the volume of the convolved chain and its occluded solvent molecules during flow to the space occupied by the true chain matter.

Flow orientation has been produced in concentrated solutions of polyundecanoates by varying the shearing stress τ. An average chain length dependence of this anomalous viscosity has been demonstrated, which provides another way of exploring the kinetic interaction of dissolved macromolecules. The solution viscosities of the polyundecanoates appear to exhibit a melt-like mechanism over a wide concentration range.

409 BROAD STREET
SUMMIT, NEW JERSEY
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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Position of Two Alicyclic Hydrocarbons in the Acidity Series[1]

BY R. D. KLEENE[2] AND G. W. WHELAND

The method of Conant and Wheland[3] and of McEwen[4] for the determination of the relative acid strengths of hydrocarbons has been extended to include phenylcyclohexane and phenylcyclopentane. The order of decreasing acid strength was found to be diphenylmethane > phenylcyclopentane > isopropylbenzene > phenylcyclohexane. No explanation is offered for the differences between the substances with only one phenyl group per molecule. The position of diphenylmethane is as expected in view of the greater possibilities for resonance in the ion.[5] An attempt to compare 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane[6] with triphenylmethane failed, as neither hydrocarbon would react at a detectable speed with the potassium derivative of the other. The trixylyl compound was shown to be a stronger acid than isopropylbenzene, however.

Experimental

Preparation of Materials.—Isopropylbenzene (cumene) was made by the method of Radziewanowski,[7] and phenylcyclohexane by the method of Kursanoff.[8] Phenylcyclopentane was prepared in 47% yield by a procedure based upon that described by Corson and Ipatieff[9] for the preparation of phenylcyclohexane; the product boiled at 68–72° at 2 mm. pressure and had an index of refraction of n^{20}_D 1.5284, in satisfactory agreement with the values in the literature.[10] Diphenylmethane was prepared by the method of Friedel and Balsohn,[11] and the 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane was the material prepared by Wheland and Danish.[6] The triphenylmethane used was the Eastman Kodak Co. product recrystallized three times from benzene.

The methyl ether of phenyldimethylcarbinol was made by the method of Ziegler, *et. al.*[12] This procedure, however, proved unsatisfactory for the methyl ethers of 1-phenylcyclohexanol and of 1-phenylcyclopentanol. These substances were made, therefore, by the method of Beaufour and of Sontag.[13]

Methyl Ether of 1-Phenylcyclohexanol.—From 50 g. of 1-phenylcyclohexanol,[14] 17 g. of sodamide, and 80 g. of methyl iodide in 150 cc. of dioxane was obtained 30 g. of the methyl ether. The product was a fragrant, colorless oil which did not solidify at −30° and did not immediately decolorize bromine in carbon tetrachloride. The physical constants were: boiling point 93–95° at 3 mm.; d^{20}_4 1.008; n^{20}_D 1.5290.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.10; H, 9.47; OCH_3, 16.3. Found: C, 81.86; H, 9.36; OCH_3, 15.8.

Methyl Ether of 1-Phenylcyclopentanol.—From 20 g. of 1-phenylcyclopentanol,[15] 5 g. of sodamide, and 30 g. of

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(1) Abstract of part of a thesis submitted by R. D. Kleene in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry, December, 1940.

(2) Present address: Chemical Warfare Service, Edgewood Arsenal, Maryland.

(3) Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

(4) McEwen, *ibid.*, **58**, 1124 (1936).

(5) Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(6) Wheland and Danish, THIS JOURNAL, **62**, 1125 (1940).

(7) Radziewanowski, *Ber.*, **28**, 1137 (1895).

(8) Kursanoff, *Ann.*, **318**, 309 (1901).

(9) Corson and Ipatieff, THIS JOURNAL, **59**, 645 (1937).

(10) Denisenko, *Ber.*, **69B**, 1353 (1936).

(11) Friedel and Balsohn, *Bull. soc. chim.*, [2] **33**, 337 (1880).

(12) Ziegler, Crössmann, Kleiner, and Schäfer, *Ann.*, **473**, 18 (1929).

(13) Beaufour, *Bull. soc. chim.*, [4] **11**, 650 (1912); Sontag, *Ann. chim.*, [11] **1**, 387 (1934).

(14) Sabatier and Mailhe, *ibid.*, [8] **10**, 546 (1907).

(15) Zelinsky, *Ber.*, **58**, 2755 (1925).

methyl iodide in dioxane was obtained 3 g. of pure ether, after the crude product had been treated with sodium-potassium alloy to remove unsaturated impurities.[16] The substance was a fragrant, colorless oil that did not solidify at −15° and did not decolorize bromine in carbon tetrachloride. Its physical constants were: boiling point 88–90° at 2 mm.; d^{20}_4 1.048; n^{20}_D 1.5483.

Anal. Calcd. for $C_{12}H_{16}O$: OCH_3, 16.3. Found: OCH_3, 16.7.

The potassium alkyls derived from isopropylbenzene, phenylcyclohexane, and phenylcyclopentane were made by the action of sodium-potassium alloy upon the corresponding methyl ethers in dry ether.[17] The yields of alkyl were in no case greater than about 50%, as determined by treatment of the reaction mixture with carbon dioxide and isolation of the resulting carboxylic acids. In the case of the potassium derivative of phenylcyclohexane, the yield was especially low (about 7–15%). This was at least partially due to the extreme slowness of the reaction between the ether and the alloy. The potassium derivatives of diphenylmethane, triphenylmethane, and 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane were prepared by the action of the potassium derivative of isopropylbenzene (prepared as above) upon the appropriate hydrocarbon. In all cases, the alkyls were treated with carbon dioxide, and the resulting acids were isolated and identified. All of these acids have been previously described, except for the one derived from the trixylylmethane.

3,3′,3″,5,5′,5″-Hexamethyltriphenylacetic Acid.—Carbonation of the bright orange-red potassium derivative of 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane yielded the corresponding acid. This formed small colorless plates melting at 276–281° with decomposition.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.82; H, 7.54; neut. equiv., 372. Found: C, 83.95; H, 7.75; neut. equiv., 375.

Comparison of Acid Strengths

Since all the alkyls which contained only one phenyl group per molecule were of nearly the same color (a dark reddish brown) the reactions could not be followed by the colorimetric method. The reaction mixtures were therefore carbonated, and the resulting acids were isolated and identified by melting point, mixed melting point, and neutral equivalent.[18]

In this way, it was found by direct comparison that phenylcyclohexane is a weaker acid than isopropylbenzene and phenylcyclopentane, that isopropylbenzene is a weaker acid than phenylcyclopentane, triphenylmethane and trixylylmethane, and that phenylcyclopentane is a weaker acid than diphenylmethane. Diphenylmethane has already been found by Conant and Wheland[3] to be a weaker acid than triphenylmethane. In all of these cases, the reactions went to completion, to within the limits of the method of analysis. On the other hand, the potassium derivative of phenylcyclopentane did not react appreciably with either phenylcyclohexane or isopropylbenzene; and the potassium derivative of neither triphenylmethane nor trixylylmethane reacted at an observable rate with the other hydrocarbon.

The micro-analyses reported in this paper were performed by Dr. T. S. Ma.

Summary

The following order of decreasing acid strength has been established: diphenylmethane > phenylcyclopentane > isopropylbenzene > phenylcyclohexane. Triphenylmethane and 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane could not be compared with each other, but both are stronger acids than isopropylbenzene.

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[16] *Cf.* ref. 12, p. 19.

[17] Ziegler and Thielmann, *Ber.*, **56**, 1740 (1923); *cf.* also ref. 12, p. 20.

[18] The procedure for the carrying out of the experiments is described in ref. 3.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Photolysis of Ketene in the Presence of Hydrogen and Methane

BY CHARLES ROSENBLUM[1]

When gaseous ketene is irradiated[2] with ultraviolet light from a quartz-mercury vapor arc, the pressure increases and the gas phase is found to contain ethylene and carbon monoxide. For short exposures these gases are present in the ratio $2CO/1C_2H_4$, whereas after longer exposures, or if ethylene is added initially, the ratio increases[2] due to polymerization of unsaturated hydrocarbon. To account for these results, mechanisms involving the primary formation of free methylene radicals have been proposed.

The evidence for the formation of free methylene radicals from ketene and other sources has been reviewed by Barrow, Pearson and Purcell.[3] As regards ketene, it is known that its ultraviolet absorption spectrum,[2,4] in the 2600–3700 Å. wave length region consists of diffuse bands characteristic of predissociation into molecular fragment; and the photochemical investigations mentioned

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[1] Present address: Merck and Co., Inc., Rahway, N. J.

[2] (a) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); THIS JOURNAL, **56**, 1644 (1934); (b) Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934).

[3] Barrow, Pearson and Purcell, *Trans. Faraday Soc.*, **35**, 880 (1939).

[4] Lardy, *J. Chim. Phys.*, **21**, 353 (1924).