with the identical results obtained by them. It was also applied similarly by Raudnitz, Schindler and Petru, *Ber.*, **68**, 1675 (1935), to the determination of the structure of aleuritic acid. More recently Mr. Daniel Swern of the Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture read a paper at the Boston meeting of the American Chemical Society on Sept. 12, 1939, entitled, "Action of Lead Tetraacetate upon Hydroxylated Oils, Fats, Fatty Acids, and Related Compounds."

RESEARCH LABORATORY
NATIONAL OIL PRODUCTS COMPANY
HARRISON, N. J.   RECEIVED DECEMBER 30, 1939

Hydrogen Fluoride as a Condensing Agent. IX.[1] Reactions of Di- and Triisobutylene with Phenol

BY J. H. SIMONS AND S. ARCHER

In connection with other work, it became necessary to determine whether or not highly branched aliphatic olefins would react with aromatic compounds to give normal or cleaved products. It is known that in the presence of large amounts of sulfuric acid, diisobutylene reacts with phenol to give cleaved products, but with small quantities of the acid the uncleaved product is obtained.[2] The same olefin reacts with toluene in liquid hydrogen fluoride to give mono and di-*t*-butyltoluene.[3]

We have found that under conditions similar to those employed by Calcott and co-workers, di- and triisobutylene both react to give *p-t*-butylphenol as the only monoalkylated phenol. However, by employing milder conditions it was possible to effect condensation without cleavage in the case of diisobutylene. By using a small amount of 70% hydrofluoric acid at 0°, *p-t*-octylphenol was isolated unaccompanied by any cleavage products. Under the same conditions dodecylphenol was not isolated when the twelve-carbon olefin was employed, although even this might be accomplished under even milder conditions.

The triisobutylene used was the so-called "lower isomer," which consists chiefly of dineopentylethylene and methylneopentyl-*t*-butylethylene. The diisobutylene was the usual commercial product, dried and redistilled, the fraction boiling at 100–103° being used.

(1) For previous paper of this series, see THIS JOURNAL, **61**, 1821 (1939).

(2) Ipatieff, Pines and Friedman, *ibid.*, **60**, 2495 (1938).

(3) Calcott, Tinker and Weinmayr, *ibid.*, **61**, 1010 (1939).

Experimental

Phenol and Diisobutylene

A. Large Quantities of Hydrogen Fluoride.—To 121 g. of hydrogen fluoride contained in a copper flask, was added a solution of 94 g. of phenol in 300 cc. of carbon tetrachloride. One mole of the olefin was dropped in with constant stirring, the reaction being kept at 0°. After twenty-four hours the reaction was stopped and then treated in the usual way. Distillation gave 88 g. of *t*-butylphenol, m. p. 97–98.5°, 14 g. of a fraction boiling at 165–185° (28 mm.), and a residue of 41 g. The higher boiling fraction did not solidify even after standing for some weeks.

B. Small Quantities of Hydrogen Fluoride.—A mixture of 20 g. of 70% hydrofluoric acid, 56 g. of the olefin, and 47 g. of phenol was kept at 0° for forty-eight hours. After the usual treatment, distillation gave 35 g. of *p-t*-octylphenol, m. p. 82–83°, and recovered phenol. When mixed with an authentic specimen there was no depression in melting point.

Phenol and Triisobutylene

A. Large Quantities of Hydrogen Fluoride.—One mole of phenol was dissolved in 300 cc. of carbon tetrachloride and added to 122 g. of hydrogen fluoride maintained at 0°. To this mixture one mole of the olefin was added slowly. After being stirred for twenty-four hours, the reaction was stopped. Removal of the solvent left a residue of 206 g. of which 64 g. boiled at 152–160° (38 mm.) and melted at 96–97°. This was *t*-butylphenol. The remainder of the material boiled over a wide range and probably consisted of the polybutylphenols.

B. Small Quantities of Hydrogen Fluoride.—Equimolar quantities of the olefin and the phenol were mixed and added to 20 g. of 70% hydrogen fluoride. After sixty hours the usual procedure was followed and the product treated with Claisen solution.[4] The latter, when examined, did not give any compound that corresponded to a dodecylphenol. When 33 g. of anhydrous hydrogen fluoride was used with 105 g. of phenol and 174 g. of the olefin, for a reaction time of fourteen hours, 52 g. of *t*-butylphenol and considerable residual phenolic material were obtained.

(4) Claisen, Eisleb and Kremers, *Ann.*, **418**, 96 (1919).

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
                    RECEIVED DECEMBER 1, 1939

Activity Coefficients in Concentrated Aqueous Solutions of Strong Electrolytes Described by Means of a Formula Containing the Mean Ionic Diameter as Single Parameter. II. Corrected Formulation

BY PIERRE VAN RYSSELBERGHE AND SYLVAN EISENBERG

In a previous paper of the same title[1] a formula with a single parameter was set up which provided

(1) P. Van Rysselberghe and S. Eisenberg, THIS JOURNAL, **61**, 3030 (1939).

a good description of the behavior of activity coefficients of concentrated aqueous electrolytes. The formula was tested successfully in a large number of cases besides those reported in our previous paper and we consider it as valuable in itself as a purely empirical contribution It has, however, no theoretical basis and we are very much indebted to Dr. H. C. Eckstrom for calling our attention to the fact that in formula (15) of this previous paper the quantity $F_{iw} = -kT \log Y$, calculated from Ursell's theory of imperfect gases should have been set equal to $N_i \Delta\mu_{iw} + N_0 \Delta\mu_{ow}$, N_0 being the number of molecules of solvent in the volume V and $\Delta\mu_{ow}$ the van der Waals contribution to the chemical potential of the solvent (other notations as in our previous paper), and not to $N_i \Delta\mu_{iw}$ alone. A complete calculation should take the solvent into account explicitly, but in our treatment it appears as the volume term. If one accepts the various other assumptions previously made, one has for the total van der Waals free energy of the solution (considered as a Gibbs free energy)

$$G_w = N_i \Delta\mu_{iw} + N_0 \Delta\mu_{ow} = kT \left[\frac{1}{2} \frac{N_i^2}{V} v + \frac{5}{64} \frac{N_i^3}{V^2} v^2 \right] \quad (1)$$

Differentiating at constant pressure, temperature and N_0, we get the following contribution to the logarithm of the average activity coefficient of the ions:

$$\log f_{\pm w} = \frac{\Delta\mu_{iw}}{kT} = \frac{1}{kT} \frac{\partial G_w}{\partial N_i}$$
$$= \frac{N_i}{V} v + \frac{15}{64}\left(\frac{N_i}{V}\right)^2 v^2 + \frac{1}{kT} \cdot \frac{\partial G_w}{\partial V} \cdot \frac{\partial V}{\partial N_i}$$
$$= \frac{N_i}{V} v + \frac{15}{64}\left(\frac{N_i}{V}\right)^2 v^2 -$$
$$\left[\frac{1}{2}\left(\frac{N_i}{V}\right)^2 v + \frac{10}{64}\left(\frac{N_i}{V}\right)^3 v^2\right]\frac{\partial V}{\partial N_i} \quad (2)$$

in which $\partial V/\partial N_i$ is the average partial molecular volume of the positive and negative ions. For the activity coefficient of the solvent we deduce similarly the contribution

$$\log f_{\pm ow} = \frac{\partial G_w}{\partial V} \cdot \frac{\partial V}{\partial N_0} =$$
$$- \left[\frac{1}{2}\left(\frac{N_i}{V}\right)^2 v + \frac{10}{64}\left(\frac{N_i}{V}\right)^3 v^2\right]\frac{\partial V}{\partial N_0} \quad (3)$$

The first effect of the correction (indicated to us by Dr. Eckstrom) is that the term in C of formula (19) of our previous paper is multiplied by 2 and the term in C^2 by 3. Our first additional term in $\partial V/\partial N_i$ may significantly affect the dependence of the activity coefficient on C^2, since v and $\partial V/\partial N_i$ are likely to be of the same order of magnitude.

In an entirely rigorous treatment one should, moreover, take into account a term containing the partial volume $\partial V/\partial N_i$ which arises from the electrostatic portion of the free energy and which is always neglected in the case of dilute solutions. The variation of dielectric constant with concentration might also be considered. We shall examine these points in the complete reinvestigation of the problem which we are planning to carry out.

Neglecting, as a provisional approximation, the terms in $\partial V/\partial N_i$ in (2), i. e., using the formula

$$\log_{10} f_{\pm w} = -0.5059 \frac{\sqrt{C}}{1 + \frac{a}{3.042}\sqrt{C}} +$$
$$2.20626 \times 10^{-3} a^3 C + 2.62692 \times 10^{-6} a^6 C^2 \quad (4)$$

we have redetermined the ionic diameters for the fifteen alkali halides studied in our previous paper, in the range of concentrations 0.1 to 3 molar. We found the following average values (in parentheses we give the definite decrease observed in all cases from 0.2 to 3 molar):

LiCl:	3.82	(3.86–3.74)
LiBr:	3.93	(3.95–3.90)
LiI:	4.29	(4.43–4.20)
NaCl:	3.31	(3.43–3.15)
NaBr:	3.53	(3.58–3.41)
NaI:	3.69	(3.75–3.58)
KCl:	2.93	(3.10–2.75)
KBr:	3.02	(3.16–2.83)
KI:	3.22	(3.38–3.00)
RbCl:	2.72	(2.75–2.55)
RbBr:	2.71	(2.85–2.58)
RbI:	2.64	(2.78–2.53)
CsCl:	2.42	(2.50–2.37)
CsBr:	2.36	(2.48–2.30)
CsI:	2.17	(2.45–1.88)

CHEMISTRY DEPARTMENT
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CAL. RECEIVED JANUARY 10, 1940