to prevent contamination of the product by the organic exchange agent when the reaction proceeds slowly despite high pot temperatures. While the reactions begin around 150° (much lower in the case of dimethyl sulfate), it is sometimes necessary to heat the mixture as high as 250° to collect the last of the product. Yields and physical properties are given in Table I.

TABLE I

REACTIONS OF SALTS OF PERFLUOROALKANOIC ACIDS

| Product[a] | Exchange agent | Yield, % | B.p., °C. | $n^{25}{}_D$[b] |
|---|---|---|---|---|
| $n$-$C_3F_7COCl$ | $C_6H_5COCl$ | 88 | 39 | 1.2852 |
| $n$-$C_3F_7COCl$ | $C_6H_5CCl_3$ | 92 | 39 | 1.2854 |
| $n$-$C_3F_7COCl$ | $p$-$CH_3C_6H_4SO_2Cl$ | 80 | 39 | 1.2851 |
| $n$-$C_3F_7COCl$[c] | $C_6H_5CCl_3$ | 87 | 39 | 1.2851 |
| $n$-$C_7F_{15}COCl$ | $o$-$C_6H_4(COCl)_2$ | 76 | 136 | 1.3035 |
| ($n$-$C_9F_{19}COCl$)[d] | $C_6H_5COCl$ | (–)[d] | (163)[d] | (1.3150)[d] |
| $n$-$C_9F_{19}COCl$ | $o$-$C_6H_4(COCl)_2$ | 88 | 173 | 1.3087 |
| $n$-$C_5F_{11}COF$ | $p$-$CH_3C_6H_4SO_2F$ | 68 | 59 | 1.2625 |
| $n$-$C_7F_{15}COF$ | $p$-$C_2H_5C_6H_4SO_2F$ | 80 | 104 | 1.2764 |
| $n$-$C_3F_7CO_2CH_3$ | $p$-$CH_3C_6H_4SO_3CH_3$ | 98 | 81 | 1.2901 |
| $n$-$C_3F_7CO_2CH_3$ | $(CH_3)_2SO_4$ | 98 | 81 | 1.2922 |

[a] The sodium salt was used in all cases but one. Amounts used varied from 5 to 50 g. The structure of the salt used corresponds to the structure of the product. [b] This is the refractive index of the "crude" product; it agrees closely with the reported value. [c] The calcium salt was used. [d] The product was contaminated with benzoyl chloride, which codistilled.

The organic exchange agent should be chosen to boil far above the desired product, as otherwise it may become a serious contaminant owing to codistillation; this results from partial immiscibility with the fluorinated product and *cannot* be overcome by increasing the efficiency of the fractionating column. Benzoyl chloride, or benzotrichloride (which forms benzoyl chloride during the reaction), may be used for synthesis of up to six-carbon perfluoroacyl chlorides, but higher ones require phthalyl chloride. In special cases, dimethyl sulfate may be used for the synthesis of close-boiling esters by the expedient of using slightly *less than equimolar* amounts; it is thereby completely converted to the salt of methylsulfuric acid, and thus does not contaminate the product.

The identity and purity of the products was well established by comparison of physical properties with literature values, and also by infrared spectroscopy; in addition, the following analytical data were secured on the "crude" products of Table I in order to lend further support to the claims of purity. The $n$-$C_3F_7COCl$,[2b,10] from the sodium salt *via* $C_6H_5CCl_3$, had a strong infrared band due to C=O at 5.52 μ.

*Anal.* Calcd. for $C_4ClF_7O$: Cl, 15.25. Found: Cl (hydr.), 15.2.

For $n$-$C_7F_{15}COCl$[2b] also, the C=O band was at 5.52 μ.

*Anal.* Calcd. for $C_8ClF_{15}O$: C, 22.2; Cl, 8.25; F, 65.9. Found: C, 22.3; Cl (hydr.), 8.3; F, 65.1.

Similarly, $n$-$C_9F_{19}COCl$[2b] had its C=O band at 5.53 μ.

*Anal.* Calcd. for $C_{10}ClF_{19}O$: C, 22.6; Cl, 6.66; F, 67.9. Found: C, 22.7; Cl (hydr.), 6.7; F, 67.2.

The sample of $n$-$C_5F_{11}COF$ had its C=O band at 5.32 μ.

*Anal.* Calcd. for $C_6F_{12}O$: C, 22.8; F(hydr.), 6.02. Found: C, 23.0; F (hydr.), 6.0.

The $n$-$C_7F_{15}COF$ showed its C=O band at 5.31 μ, and was, therefore, not further analyzed. There was no question as to the identity of the $C_3F_7CO_2CH_3$,[11] which is a well-known compound.

**Acknowledgment.**—The author thanks Dr. W. E. Keiser and Dr. J. J. McBrady for the infrared spectral analysis.

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# Alkaline Hydrolysis of Ethyl Benzoate in Aqueous Dimethyl Sulfoxide

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The data presented in the recent review article of Parker[1] very clearly demonstrate the marked rate-enhancing ability of dipolar aprotic solvents such as dimethyl sulfoxide upon bimolecular displacement reactions effected with anions. Thus Friedman and Shechter[2] reported the greatly accelerated displacement of halide by cyanide, azide, thiocyanate, and halide ions; Smiley and Arnold[3] observed the facile interconversion of primary and secondary halides to nitriles by the action of cyanide ion in dimethyl sulfoxide; and Cram and co-workers[4] found that use of dimethyl sulfoxide as a solvent allows both the Wolff–Kishner reduction and the Cope elimination reaction to be run at room temperature.

In accordance with these findings and his own excellent work with SNAr-type reactions, Parker[5a] postulated that any bimolecular reaction of a small anion passing through a large polarizable transition state will be considerably accelerated in the change from protic to dipolar aprotic solvents.

Such a reaction that has yet to be investigated kinetically in dipolar aprotic solvents is the alkaline hydrolysis of esters.[5b] In consideration of the large amount of work that has been carried out towards elucidating the mechanism of ester saponification ($BAc^2$),[6,7] a quantitative study of the effect of an aprotic solvent upon this reaction should be of interest. To this end, the present paper deals with the alkaline hydrolysis of ethyl benzoate in aqueous dimethyl sulfoxide. This ester was selected for study because a similar investigation carried out with ethyl benzoate in aqueous ethanol permits a comparison with a typical protic solvent system.

Table I presents the kinetic findings of this work. It is readily apparent from this table that alkaline hydrolysis of ethyl benzoate in aqueous dimethyl sulfoxide is accelerated relative to aqueous ethanol. Since the mechanism of the base-catalyzed hydrolysis of a normal ester[6,7] involves the production of a large polarizable transition state *via* the rate-determining addition of hydroxide ion to the carbonyl carbon atom of the ester, the data reported in Table I are in accord with Parker's postulate. Change from aqueous ethanol to aqueous dimethyl sulfoxide leads to a diminishment in hydroxide ion solvation[1,8] and an increase in transition state

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(1) A. J. Parker, *Quart. Rev.*, (London) **16**, 163 (1962).

(2) L. Friedman and H. Shechter, *J. Org. Chem.*, **25**, 877 (1960).

(3) R. A. Smiley and C. Arnold, *ibid.*, **25**, 257 (1960).

(4) D. J. Cram, M. Sohyum, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

(5) (a) A. J. Parker, *J. Chem. Soc.*, 1328 (1961). (b) NOTE ADDED IN PROOF.—E. Tommila and co-workers [*Acta Chim. Scand.*, **17**, 1957, 1980 (1963)] have recently reported a similar rate-enhancing influence of dimethyl sulfoxide in the saponification of ethyl acetate.

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(7) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).

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TABLE I

RATES OF ALKALINE HYDROLYSIS OF ETHYL BENZOATE IN AQUEOUS DIMETHYL SULFOXIDE

| Solvent, % by vol. | Temp., °C. | $k_2 \times 10^4$ l./mole/sec. | Rel. rate |
|---|---|---|---|
| 85% aq. EtOH | 25.0 | 7.0[a] | 1 |
| 85% aq. DMSO[b] | 25.0 | 2240 ± 80[c] | 320 |
| | 20.0 | 1550 ± 50 | |
| | 15.0 | 1050 ± 15 | |
| | 10.0 | 735 ± 20 | |
| 80% aq. DMSO | 25.0 | 1140 ± 34 | 160 |
| | 20.0 | 810 ± 20 | |
| | 15.0 | 550 ± 20 | |
| | 10.0 | 385 ± 30 | |
| 75% aq. DMSO | 25.0 | 660 ± 27 | 94 |
| | 20.0 | 480 ± 8 | |
| | 15.0 | 350 ± 35 | |
| | 10.0 | 250 ± 15 | |
| 70% aq. DMSO | 30.0 | 700 ± 28 | |
| | 25.0 | 500 ± 14 | 71 |
| | 20.0 | 350 ± 9 | |
| | 15.0 | 250 ± 6 | |
| 65% aq. DMSO | 35.0 | 770 ± 10 | |
| | 30.0 | 535 ± 15 | |
| | 25.0 | 380 ± 26 | 54 |
| | 20.0 | 270 ± 7 | |
| | 15.0 | 180 ± 16 | |

[a] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937). [b] Dimethyl sulfoxide. [c] One standard deviation unit.

TABLE II

THERMODYNAMIC ACTIVATION PARAMETERS FOR ALKALINE HYDROLYSIS OF ETHYL BENZOATE IN AQUEOUS DIMETHYL SULFOXIDE

| Solvent | Mole fraction of organic component | $\Delta H^*$, cal./mole | $\Delta S^*$, e.u. |
|---|---|---|---|
| Aq. EtOH[a] | 0.334 | 15,490 | −19.2 |
| | 0.444 | 16,020 | −19.0 |
| | 0.493 | 16,400 | −17.0 |
| | 0.690[b] | 17,320 | −15.8 |
| | 0.850 | 18,420 | −12.4 |
| Aq. DMSO | 0.320 | 11,700 ± 240[c] | −26 ± 3 |
| | 0.372 | 11,500 ± 120 | −26 ± 1 |
| | 0.433 | 10,200 ± 300 | −30 ± 3 |
| | 0.504 | 11,200 ± 400 | −25 ± 4 |
| | 0.591 | 12,200 ± 250 | −21 ± 3 |

[a] Obtained from data of ref. 10. [b] C. A. Burkhard and R. E. Burnett, *J. Am. Chem. Soc.*, **80**, 341 (1958). [c] One standard deviation unit from the mean.

solvation[5] with concomittant decrease in free energy of activation.

The data in Table II reveal that substitution of aqueous dimethyl sulfoxide for aqueous ethanol leads to both a reduced entropy and enthalpy of activation with the enthalpic change controlling the free energy of activation in agreement with the Hughes–Ingold theory of solvent effects on reaction kinetics.[9] Although the small differences in activation parameters provide only a slight basis for an anomalous dependency of activation enthalpy upon the mole fraction of dimethyl sulfoxide, such speculation is tempting. Further work is planned in this area to describe more adequately the solvation mechanism.

## Experimental

**Preparation of Materials.**—Ethyl benzoate ($n^{20}_D$ 1.5048) was purified by fractional distillation and analysis by g.l.p.c. gave only a single sharp peak. Dimethyl sulfoxide was dried over 4A Molecular Sieves and analysis by g.l.p.c. did not reveal the presence of any significant amount of impurity. The dimethyl sulfoxide–water—sodium hydroxide mixtures were prepared according to the following scheme: a weighed quantity of sodium hydroxide was dissolved in a measured volume of water which in turn was diluted with measured volumes of dimethyl sulfoxide to give, respectively, 65, 70, 75, 80, and 85% (by volume) aqueous dimethyl sulfoxide solutions approximately 0.05 $N$ in sodium hydroxide. In all cases, mixing dimethyl sulfoxide with water produced a shrinkage of the total volume.

**Rate Measurements.**—The kinetic experiments were carried out using both ester and sodium hydroxide in equal concentrations (about 0.05 $M$). The ester was weighed out in a volumetric flask, placed in a constant temperature bath (accurate to ±0.1°), and rapidly brought up to volume with the appropriate solvent mixture (pre-equilibrated to the reaction temperature, zero time was recorded as the time when one-half the solvent had been added). Aliquots were removed periodically; the reaction was quenched by addition to an excess of aqueous hydrochloric acid of known normality, and finally back-titrated with standardized aqueous sodium hydroxide to a bromthymol blue end point. The values of $k_2$ were calculated from the second-order reaction rate equation

$$k_2 = x/at\,(a - x)$$

where $a$ is the initial concentration of each reactant and $a - x$ is the concentration of each reactant at time $t$. All of the measured reactions followed strictly second-order kinetic law, and consumed, within experimental error, 100% of the base present.

**Treatment of the Kinetic Data.**—The thermodynamic activation functions were obtained by IBM 1620 computer regression analysis of ln $k/T$ vs. $1/T$.

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(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345-350.

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# Preparation of Tetracyclopropyllead and a Study of Some of Its Cleavage Reactions

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Research in organometallic chemistry hasl ead to the discovery of many well-known aliphatic and aromatic lead compounds. Organometallic compounds containing small groups such as the vinyl and cyclopropyl have aroused much interest in the past few years. Tetravinyllead has been prepared[1]; moreover, vinyl metal compounds have been extensively studied with examples having been prepared for common metals in all the A families of the periodic table. Although larger cycloalkyllead compounds have been reported,[2,3] the preparation of tetracyclopropyllead could not be found in the literature. Only a few cyclopropylmetal compounds have been reported, among which are cyclopropyllithium,[4] cyclopropylmagnesium bromide,[5] and dicyclopropylmercury.[6] Recently, some cyclopropyl compounds of the group IV elements—silicon, germanium, and tin—have been prepared.[7]

We have prepared the last cyclopropyl organometallic compound of the group IV-A family, tetracyclopro-

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