Heats of Mixing in Solid Solutions of Benzoic Acid and *m*-Fluorobenzoic Acid

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Heats of neutralization in basic methanol-water solution were determined for benzoic acid, *m*-fluorobenzoic acid, and solid solutions of the two at 25° C. Heats of mixing calculated from these data show a maximum of 350 ± 20 cal. per mole near 0.4 mole fraction of benzoic acid.

BENZOIC ACID and *m*-fluorobenzoic acid have been shown (*1*) to form solid solutions miscible in all proportions. The other two monofluorobenzoic acids have miscibility gaps in their solid solutions with benzoic acid. As a first step in the study of solid solutions, the authors determined the heats of mixing in the benzoic acid–*m*-fluorobenzoic acid system. Since the direct measurement of this heat is impractical, an indirect method was necessary. Solution calorimetry, with its high precision and relative ease of operation, is the best possible tool for such a study. Choice of a calorimetric reaction scheme must be based on the following criteria: All of the interactions between the components of the solid solution must be destroyed in the reaction; the molar heat of reaction must be small enough so that the experimental uncertainty is small, relative to the heat of mixing, yet large enough so that sufficiently small samples may be used to avoid violation of the above criterion; and the calorimetric fluid should be easily and reproducibly prepared. The observed heats should be fairly insensitive to slight variations in the preparation of this solvent. The neutralization reaction in 50% (volume) methanol-water containing 0.10*M* NaOH best satisfied these criteria. Sample sizes range from 5 to 10 mmoles. The heat of neutralization was found to be independent of sample size within this range and was not affected by the addition of 20 mmoles of the conjugate base of either acid to the solvent mixture, indicating that the first criterion is satisfied.

EXPERIMENTAL

The calorimeter consists of a 300-ml. silvered glass Dewar flask to which a chrome-plated brass flange is secured with epoxy cement. This flange, with a silicone rubber gasket, bolts to a chrome-plated brass lid to which two 5-mm. i.d. Trubore glass bearings (Ace Glass), a glass tube for thermistors, and a spiral glass tube for the heater are cemented. This plate is suspended by the glass bearings from a larger aluminum plate, which is itself suspended from a larger plate serving as mount for the stirrer. This entire unit is surrounded by a metal submarine and suspended in an oil bath. The solution in the Dewar flask is stirred by glass propellers on a Trubore shaft powered by a 500-r.p.m. motor. Samples of solids are weighed in fragile glass ampoules (5 ml.) which are taped to the other Trubore shaft and sealed with paraffin. The reaction is initiated by depressing the shaft, thereby crushing the ampoule against a spur mounted on the heating coil. The heat evolved on crushing an empty bulb is 0.09 ± 0.02 cal. The heat capacity of the system is determined for each measurement with a 325.74-ohm Manganin heater mounted in the glass spiral filled with transformer oil. The thermometer circuit consists of two thermistors (YSI, 10,000 ohms at 25° C.) comprising opposite arms of a Maier bridge (*2,3*), the other arms consisting of fixed 10,000-ohm resistors. The bridge input potential is maintained constant at 1.0000 volt and the out of balance potential is measured with a Keithley Model 660A differential voltmeter with a sensitivity of 2 μv. This potential is essentially linear with temperature in the vicinity of 25° C. with a coefficient of about 20 mv. per degree. All measurements were made at 25.0° ± 0.1° C.

Reagent grade benzoic acid and *m*-fluorobenzoic acid (Eastman) were sublimed and further purified by two fractional crystallizations, the higher melting one third being

Table I. Heats of Neutralization of Benzoic Acid, *m*-Fluorobenzioc Acid, and Their Solid Solutions in 50% Methanol-Water and Calculated Heats of Mixing at 25° C.

X_B	ΔH_1, Cal./Mole	ΔH^{mix}, Cal./Mole
0.0000	−1643 ± 5	0
0.1218	−1887 ± 8	165 ± 10
0.2509	−2076 ± 15	268 ± 16
0.3639	−2236 ± 10	353 ± 12
0.4964	−2311 ± 8	340 ± 11
0.6269	−2341 ± 8	284 ± 11
0.7510	−2386 ± 2	246 ± 7
0.8672	−2367 ± 12	151 ± 14
1.0000	−2305 ± 7	0

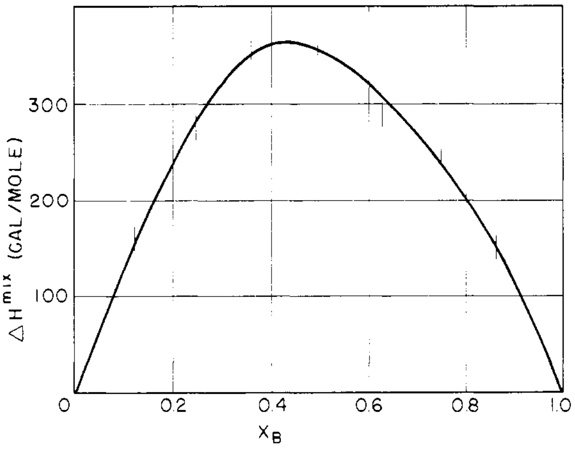

Figure 1. Heats of mixing in solid solutions of benzoic acid and *m*-fluorobenzoic acid at 25° C.

retained each time. No differences could be observed in the heats of neutralization of samples taken after one and two crystallizations.

Solid solutions were prepared by several methods to test the reproducibility of the preparations. For all the results reported here, samples were prepared by dissolving known amounts of the two acids in ether and evaporating to dryness, as these samples gave the fastest rates of solution and more reproducible heats. No differences in the heats of neutralization could be detected with samples crystallized at different rates, or between the first and last fractions of the crystallization. Some samples were prepared by fusion of known amounts of the acids and slow crystallization at the melting point, while others were fused at temperatures above the melting point and quickly crystallized by pouring the liquid on a cold glass plate. These samples gave heats in excellent agreement with those recrystallized from ether, though less reproducible because of lower rates of solution and possibly some changes in composition through sublimation. Fusion at temperature greater than 150° C. produced samples with lower heats of neutralization. The causes of this effect were not investigated.

RESULTS

The calorimetric reaction scheme is given by reactions 1 and 2, where X_B is mole fraction of benzoic acid and the symbol (*) is used to indicate that the preceding species is dissolved in the solvent mixture, 50% (volume) methanol-water.

$$[X_B\,\mathrm{BH} + (1 - X_B)m\mathrm{FBH}]\ (\mathrm{solid}) + \mathrm{OH}^-\ (*) = X_B\,\mathrm{B}^-\ (*) + (1 - X_B)m\mathrm{FB}^-\ (*) + \mathrm{H_2O}\ (*) \qquad (1)$$

$$\mathrm{BH(s)} + \mathrm{OH}^-\ (*) = \mathrm{B}^-\ (*) + \mathrm{H_2O}\ (*) \qquad (1a)$$

$$m\mathrm{FBH(s)} + \mathrm{OH}^-\ (*) = m\mathrm{FB}^-\ (*) + \mathrm{H_2O}\ (*) \qquad (1b)$$

$$X_B\,\mathrm{BH(s)} + (1 - X_B)m\mathrm{FBH(s)} = [X_B\,\mathrm{BH} + (1 - X_B)m\mathrm{FBH}]\ (\mathrm{solid}) \qquad (2)$$

$$\Delta H_2 = X_B \Delta H_{1a} + (1 - X_B)\ \Delta H_{1b} - \Delta H_1 = \Delta H^{\mathrm{mix}}$$

Reactions 1a and 1b are recognized as special cases of Reaction 1 when X_B has the values 1 and 0. The measured heats of neutralization and the calculated heats of mixing are given in Table I. Each listed value is the average of at least two independent measurements, and the uncertainties are the maximum deviation from the mean. Figure 1 shows that the heat of mixing reaches a maximum value of about 350 cal. per mole around $X_B = 0.4$.

Similar studies on the partially miscible systems of benzoic acid and *o*- and *p*-fluorobenzoic acids are now in progress.

LITERATURE CITED

(1) Claeson, G., Bäckstrom, R., *Arkiv Kemi* **15**, 241 (1960).
(2) Maier, C.G., *J. Phys. Chem.* **34**, 2860 (1930).
(3) O'Hara, W.F., Wu, C.H., Hepler, L.G., *J. Chem Educ.* **38**, 512 (1961).

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Trinitromethane Adducts of α,β-Unsaturated Aldehydes and Acylals

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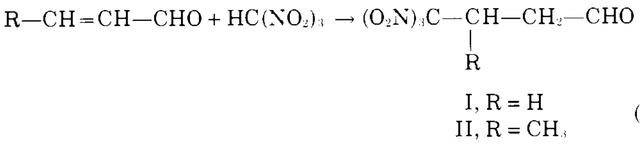
The Michael addition of trinitromethane to α,β-unsaturated aldehydes and acylals yielded the corresponding trinitroaldehydes and trinitroacylals in good yield. Physical properties of the compounds are given. A facile synthesis for 4,4,4-trinitrobutyraldehyde is reported.

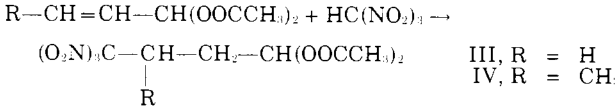
ALTHOUGH the Michael addition of trinitromethane to α,β-unsaturated compounds has been studied extensively (*1, 5-7*), there have been no reports of polynitroaliphatic aldehyde derivatives prepared by this method. Ostensibly, Schimmelschmidt (*7*) obtained 3-methyl-4,4,4-trinitrobutyraldehyde by trinitromethane addition to the ethylenic and carbonyl groups of crotonaldehyde, followed by regeneration of the aldehyde group by sodium bicarbonate; however, no experimental details or physical properties were given. Since the authors were interested in polynitroaliphatic aldehyde derivatives, the Michael addition of trinitromethane to unsaturated aldehydes and acylals was investigated, and the previously unreported 4,4,4-trinitrobutyraldehyde and similar compounds were successfully prepared by facile syntheses.

Trinitromethane underwent Michael addition to acrolein and crotonaldehyde in aqueous and chloroform solvent, Equation 1, to give good yields of 4,4,4-trinitrobutyraldehyde, I, and 3-methyl-4,4,4-trinitrobutyraldehyde, II.



$$\mathrm{R{-}CH{=}CH{-}CHO + HC(NO_2)_3 \rightarrow (O_2N)_3C{-}\underset{\displaystyle R}{\underset{|}{C}}H{-}CH_2{-}CHO} \qquad \begin{matrix}\mathrm{I,\ R = H}\\ \mathrm{II,\ R = CH_3}\end{matrix} \qquad (1)$$

The addition of trinitromethane to 1,1-diacetoxy-2-propene and to 1,1-diacetoxy-2-butene was also successful, Equation 2, and gave the Michael adducts, 1,1-diacetoxy-4,4,4-trinitrobutane, III, and 1,1-diacetoxy-3-methyl-4,4,4-trinitrobutane, IV.



$$\mathrm{R{-}CH{=}CH{-}CH(OOCCH_3)_2 + HC(NO_2)_3 \rightarrow (O_2N)_3C{-}\underset{\displaystyle R}{\underset{|}{C}}H{-}CH_2{-}CH(OOCCH_3)_2} \qquad \begin{matrix}\mathrm{III,\ R = H}\\ \mathrm{IV,\ R = CH_3}\end{matrix} \qquad (2)$$

Both aqueous and nonaqueous solvents such as chloroform have been used as media for addition reactions of tri-