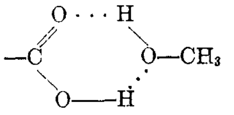
large red shifts obtained for nitrophenols[1] and aninophenols. For the other groups the order, Br > CH_3 > $N(CH_3)_2$ > OCH_3, for blue shifts suggests that the acidity of the acid and hence the hydrogen-donor properties of the COOH may in part be involved. The largest blue shifts were obtained for methanol with *p*-bromobenzoic and *p*-N,N-dimethylaminobenzoic acids. For the latter, solvation of the dimethylamino group could explain this effect. However, the results for bromo must be considered on the basis of solvation of the carboxyl only. This may involve a hydrogen-bonding structure of type D, in which the bonding between the alcohol hydrogen and the carboxyl carbonyl acts to bring the alcohol oxygen in close proximity to the carboxyl hydrogen. The latter type of bonding builds up the electron density at the substituent carbon and hinders charge-transfer states of the carboxyl. Ito[18] has observed a similar effect for benzoic acid in ether.



D

In summary, a study of the solvent shifts for anilines, benzoic acids, and (previously) nitrobenzenes suggest that (a) hydrogen bonding from solute to solvent in which substituent atom contains filled orbitals (*i.e.*, NH_2 and OH) leads to red shifts, (b) hydrogen bonding from solute to solvent in which a substituent atom contains an empty orbital or electron-deficient atom (*i.e.*, COOH) leads to blue shifts, (c) hydrogen bonding from solvent to solute which prevents substituent orbitals from overlapping ring orbitals (*i.e.*, NH_2 and OCH_3) leads to blue shifts, and (d) strong hydrogen-bonding effects tend to cover up other effects such as dielectric constant and index of refraction.

Experimental Section

Absorption spectra in the region 220–350 mμ were obtained using a Bausch and Lomb automatic recording ultraviolet spectrophotometer, Model 505, with a constant 5-A band width and 1-cm matched silica cells. After each determination the instrument was calibrated against the 253.7- and 313.1-mμ lines of mercury. Cyclohexane, dioxane, methanol, and propanol-2 were obtained as Spectraquality solvents (Matheson Scientific Co.). Propanol-1 and *t*-butyl alcohol were purchased as highest purity reagents, dried, and distilled through a 24-in. spinning-band column until no impurity bands were obtained when the solvent was passed through a 10-ft Carbowax column in a Wilkens Aerograph gas chromatograph. Concentrations used were 2×10^{-5} to 7×10^{-5} *M* with a scan time of 10 min.

The anilines were purchased as the highest purity compounds available and in most cases were recrystallized or distilled until the physical properties agreed with literature values, after which each was dried in an Abderhalden apparatus for 3 hr.

p-Aminobenzonitrile was prepared by the method of Friedman and Schecter[19] from *p*-bromoaniline. *p*-Phenoxyaniline was prepared by reduction of 4-nitrodiphenyl ether by the method of Suter.[20] The ethyl esters of *o*-, *m*-, and *p*-aminobenzoic acids were prepared by refluxing the respective acid with ethanol saturated with dry hydrogen chloride.

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[18] M. Ito, *J. Am. Chem. Soc.*, **82**, 1559 (1960).

[19] L. Friedman and H. Schecter, *J. Org. Chem.*, **26**, 2522 (1961).

[20] C. M. Suter, *J. Am. Chem. Soc.*, **51**, 2581 (1929).

On the Supposed Resolution of 2-Bromobutane

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It has been claimed that racemic 2-bromobutane has been successfully resolved by gas chromatography on an optically active substrate.[1] In an attempt to repeat this work, we have observed dehydrohalogenation of 2-bromobutane to mixed butenes in the injection port of the chromatograph.

1-Butene and *cis*- and *trans*-2-butene have been identified by comparison of retention time and of infrared spectrum (*trans* only) with those of authentic samples. The extent of decomposition varies with the temperature of the injection port (Figure 1).

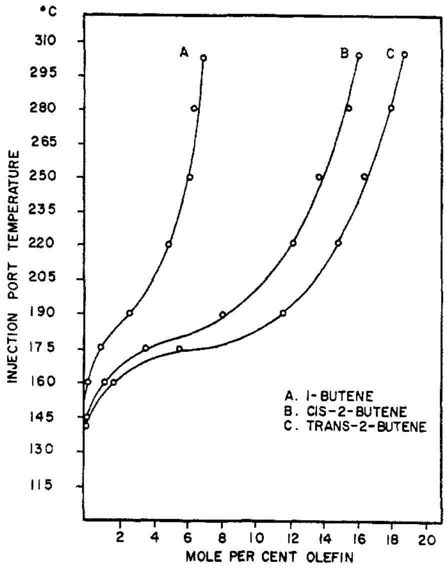

Figure 1.—Plot of temperature *vs.* amount of each decomposition product for *sec*-butyl bromide

Since other workers[2,3] have failed in attempts to resolve 2-bromobutane by gas chromatography, we feel that our results may explain Karagounis' apparent success. The similarity of our chromatograms of the butenes to Karagounis' published separation (note *three* peaks) confirms this conclusion.

Two further observations, we believe, led to Karagounis' claim for resolution. The comparative study using an optically inactive substrate [polyglycol on firebrick] led to a single "unresolved" peak. This single peak resulted from the failure of this column to resolve olefins. The second observation concerned the area of the major peaks (*cis*- and *trans*-2-butene). These were, unfortunately, of approximately equal area as one would expect in a successful resolution.

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[1] G. Karagounis and G. Lippold, *Naturwissenschaften*, **46**, 145 (1959).

[2] G. Goldberg and W. A. Ross, *Chem. Ind.* (London), 657 (1962).

[3] N. A. Goeckner, *Dissertation Abstr.*, **19**, 3127 (1959).

Experimental Section

The chromatograph employed in the investigation was an F and M Model 300 with thermal conductivity detector. All chromatograms were obtained under isothermal column conditions. The column used was $^3/_{16}$ in. × 20 ft copper tubing filled with 100–200 mesh activated alumina coated with 20 wt % diethyl D-tartrate. Helium was the carrier gas and flow rate was maintained at 25 cc/min. The column was operated at 90°. These conditions essentially duplicate those of Karagounis.

Some resolutions have been reported subsequent to the original work of Karagounis,[4,5] but these involved the use of metal complexes. Most other resolutions by gas chromatography reported in the literature deal with the separation of diastereoisomers.

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[4] G. Karagounis and E. Lemperly, *Z. Anal. Chem.*, **189**, 131 (1962).

[5] R. E. Sievers, R. W. Moshier, and M. L. Morris, *Inorg. Chem.*, **1**, 966 (1962).

Dimethyl Sulfoxide as a Solvent for the Lossen Rearrangement

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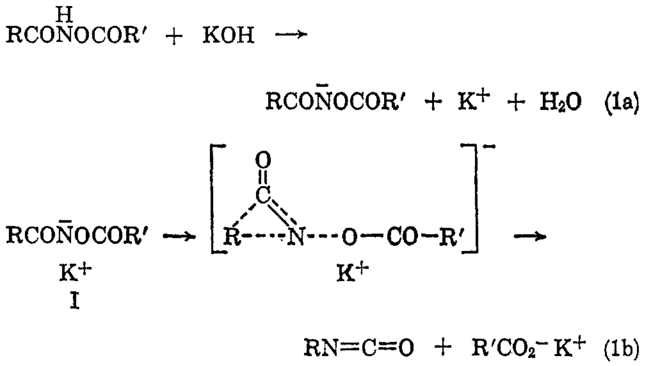
Numerous examples of rate acceleration by use of dimethyl sulfoxide in place of protic solvents in bimolecular second-order reactions of anions with neutral substrates are well known.[1] We now wish to report moderate rate acceleration by use of dimethyl sulfoxide solvent in place of 0.1 N ammonia for three out of four cases for the Lossen rearrangement (eq 1b), a *unimolecular first-order* reaction of an anion (I).



$$\mathrm{RCO\overset{H}{N}OCOR' + KOH \longrightarrow RCO\bar{N}OCOR' + K^+ + H_2O} \quad \text{(1a)}$$

$$\mathrm{RCO\bar{N}OCOR'\ K^+\ (I) \longrightarrow [\ ]^- \ K^+ \longrightarrow RN{=}C{=}O + R'CO_2^-K^+} \quad \text{(1b)}$$

The accepted mechanism[2-4] for this reaction is as shown above; migration of R occurs simultaneously or nearly simultaneously with the heterolytic cleavage of the hydroxamate anion (the transition state is represented by the species enclosed in brackets). Rate results obtained with dimethyl sulfoxide (DMSO) as a solvent are listed in Table I and are compared with the results of previous workers[2,3] who used 0.1 N ammonia as solvent.

The normal course of the Lossen rearrangement (eq 1b) in dimethyl sulfoxide was shown to obtain by trapping the isocyanate *via* reaction with *n*-butylamine (see Experimental Section).

Incomplete dissociation of the salts used in the rate measurements would influence the observed rates. Electrical conductance measurements were therefore made on potassium benzoyl *p*-methylbenzhydroxamate solutions at 25° to allow comparison with literature conductance data[5] for dimethyl sulfoxide solutions. The two lowest concentrations in Table II correspond to the concentration ranges previously used in determining the conductivity of numerous salts in dimethyl sulfoxide[5]—these salts were shown to be completely dissociated in the concentration ranges studied.[5] The equivalent conductances reported in Table II for the two lowest concentrations of potassium benzoyl *p*-methylbenzhydroxamate vary with concentration in the same manner as the equivalent conductances of the salts previously shown to be completely dissociated in this concentration range; therefore, it is highly likely that potassium benzoyl *p*-methylbenzhydroxamate is largely dissociated at these low concentrations. Further, since the equivalent conductances of this potassium salt do not change markedly upon going to higher concentrations, it is likely that it is largely dissociated at these concentrations (those used in the kinetic studies). The salts in Table I with R = phenyl or *m*-methylphenyl should be dissociated to extents comparable to that for R = *p*-methylphenyl. For R = *o*-methylphenyl, however, steric hindrance to solvation of the anion may be sufficient to reduce the extent of dissociation compared to the other salts; consequently, no conclusion as to the extent of dissociation of this *ortho* derivative can be drawn from the present data. Conductance measurements are rendered difficult in this system for two reasons: one, the Lossen rearrangement commences when the salt is dissolved and, two, the rate of solution of the salt is slow—very slow in the case of the *o*-methyl derivative—with the result that a significant portion of the salt will have reacted (eq 1b) before all of the salt has been dissolved (the conductance measurements will thus be affected but not the kinetics, since the rates are first order).

The general explanation[1a] offered for the acceleration of bimolecular reactions between anions and neutral substrates upon change from protic to dipolar aprotic solvents is applicable to the salts (except R = *o*-methylphenyl) in Table I if the transition state for the Lossen reaction has greater charge dispersal (which is likely) than the initial state. As has been recently discussed,[1c] however, rate acceleration by use of dimethyl sulfoxide in place of hydroxylic solvents is complicated and probably the result of several factors. The markedly different relative rate in Table I for R = *o*-methylphenyl *may* be due to incomplete dissociation of the salt in dimethyl sulfoxide; the proximity of the positive potassium ion to the negative charge delocalized over the amide-like portion of anion I would be expected to retard the formation of the carboxylate ion from I.

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[1] See, for example: (a) A. J. Parker, *Quart. Rev.* (London) **16**, 163 (1962); (b) D. D. Roberts, *J. Org. Chem.*, **29**, 2039 (1964); (c) C. A. Kingsbury, *ibid.*, **29**, 3262 (1964); (d) E. Tommila and M. Murto, *Acta Chem. Scand.*, **17**, 1947 (1963).

[2] R. D. Bright and C. R. Hauser, *J. Am. Chem. Soc.*, **61**, 618 (1939).

[3] W. B. Renfrow, Jr., and C. R. Hauser, *ibid.*, **59**, 2308 (1937).

[4] P. A. S. Smith, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 528–541.

[5] P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.* **60**. 1433 (1956).