Anal. Calcd. for $C_{30}H_{22}Br_2O_8$: C, 58.3; H, 3.84. Found: C, 58.8; H, 4.04.

4′-Methoxy-2,2,2-trianisylacetophenone (III) from the Interaction of Tetraanisylethylene (I) with Chlorine.—An ethylene chloride solution containing 0.893 g. (1.97×10^{-3} mole) of I and 2.3×10^{-3} mole of chlorine was allowed to stand in diffuse daylight for two days. The yellow solution was concentrated by distillation under reduced pressure to give an orange residue. Crystallization from ethyl alcohol-benzene and then from absolute ethyl alcohol gave 0.20 g. (22%) of III, m.p. 138–140°. Further crystallization sharpened the m.p. to 139–140°. A mixed m.p. with authentic III showed no depression.

Many other similar experiments with other electron acceptors and I were tried but no product other than I could be isolated.

Spectrophotometric Measurements.—Visible and ultraviolet absorption spectra were determined using a Cary model 11 recording spectrophotometer. A set of matched silica cells of path length 1.00 ± 0.01 cm. were used to determine the spectra. Some measurements were made in cells of longer path length of comparable precision.

All infrared spectra were obtained using a Perkin-Elmer model 21 infrared spectrophotometer equipped with a sodium chloride prism. Many of the measurements were made using matched pairs of fixed liquid cells of 0.025-, 0.10- and 1.0-mm. path length. Two special cells containing no metal parts in contact with the solution were also used.[19]

Solutions of model compounds of satisfactory concentrations were made up in suitable solvents. Concentrations ranging from 10^{-3} to 10^{-5} M were used for most measurements in the visible and ultraviolet region. Concentrations from about 1 to 10^{-2} M were used in the infrared region. In the studies on the complexes and the reaction mixtures stock solutions were prepared for convenience in mixing solutions of various compositions. In some experiments the measurements had to be made on freshly prepared solutions; for others aging of the solutions was necessary. For the experiments requiring the removal of the electron acceptor at some stage excess copper bronze was used to remove halogens and aqueous bicarbonate was used to remove proton donors. In all of these experiments a wide latitude of operations was possible. After each removal of reagent or addition of reagent it was possible to measure spectra in whichever region desired for the purpose of identifying species present in the solution.

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[19] W. B. Person, R. E. Erickson and R. E. Buckles, *J. Chem. Phys.*, **27**, 1211 (1957).

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Solvation Effects and Relative Rates. II. Some Benzyl Chlorides in Methanol[1]

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A general analysis of solvation effects and relative rates, with particular attention to the problem of the effect of structure upon reactivity, is presented and is applied to the solvolysis reactions of some benzyl chlorides in methanol. Data for the analysis are presented, being obtained from measurements of the rates of solvolyses of benzyl, *p*-methylbenzyl and *p*-*t*-butylbenzyl chlorides, of the vapor pressures of the pure chlorides, and of the Henry's law constants for the chlorides in solution, all at 25.06°. It is observed that the relative reactivities of the *p*-methylbenzyl and *p*-*t*-butylbenzyl chlorides lie in the Baker–Nathan sequence, but it is pointed out that differential solvation effects make ambiguous any interpretation of this sequence in terms of "intrinsic" reactivity.

Introduction

Most reactions of interest to organic chemists occur in solution. In such reactions solute-solvent interactions (solvation effects) are inherent in the reacting systems and in the values of the specific rate constants observed. If one is concerned with an interpretation of the effect of structure or of reaction medium upon the rate of a reaction, these solvation effects introduce serious complications, for they operate both with the reactants and with the critical complex and need not be identical for different structures or media. For the purpose of isolating solvation effects from "intrinsic" reaction rates, it is useful to analyze rate data in terms of idealized gas-phase reactions where intermolecular interactions are at a minimum. An analysis appropriate to our studies of solvation effects and relative rates is outlined here for the usual situation where all reactants are incorporated in the critical complex.

The energetics of interest in defining the rate of a reaction may be represented schematically as in Fig. 1 which is similar to the representation of Winstein and Fainberg.[2] The free energies of activation, ΔF_s^* and ΔF_g^*, are differences in standard free energies and represent the changes in free energies associated with the transfer from the ground states to the transition states of the moles of reactants necessary for the formation of one mole of critical complex, all species being in their standard states of concentration. Specific rate constants in solution and in the gas phase depend upon these free energies and are given, according to the absolute rate equation,[3] by equations 1 and 2, respectively. The magnitudes of the specific rate

$$k_s = (kT/h)e^{-\Delta F^*_s/RT} \qquad (1)$$

$$k_g = (kT/h)e^{-\Delta F^*_g/RT} \qquad (2)$$

constants and of the free energies of activation depend upon the choice of standard states. These are defined, implicitly, as hypothetical unit concentrations in the concentration dimensions of the specific rate constants. Thus, the standard states represented by the energy levels in Fig. 1 are normally defined by the values (and dimensions) of the specific rate constants as experimentally determined.[4] Where desirable, however, alternative

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[1] For the previous paper in this series see, R. A. Clement and M. R. Rice, THIS JOURNAL, **81**, 326 (1959); for a preliminary report of some of this work, see R. A. Clement and J. N. Naghizadeh, *ibid.*, **81**, 3154 (1959).

[2] S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

[3] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 13, 14.

[4] For unimolecular reactions, specific rate constants have no concentration dimensions and are, as are the associated free energies of activation, independent of the choice of standard states. In these cases, the standard states represented by the energy levels in Fig. 1 must be defined, explicitly.

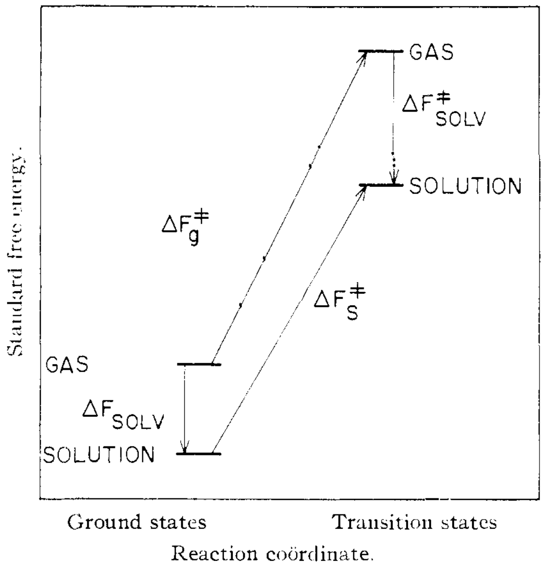

Fig. 1.—Schematic representation of the energetics of a reaction in the gas phase and in solution.

standard states may be employed if appropriate changes are made in the values (and dimensions) of the observed specific rate constants and in the magnitudes of the free energies of activation.[5] The free energy differences, ΔF_{solv} and ΔF^*_{solv}, are solvation energies and represent the changes in free energies associated with the transfer of the appropriate species from their standard states in the gas phase to their standard states in solution. Like ΔF^*_s and ΔF^*_g, the magnitudes of ΔF_{solv} and ΔF^*_{solv} depend upon the choice of standard states.

If one is interested in an "intrinsic" reaction rate which is isolated from solvation effects or, indeed, from all types of general intermolecular interactions, the relevant specific rate constant is k_g as defined in equation 2. In view of relationship 3, obtained from Fig. 1, and of the identity of equation 1, k_g

$$\Delta F^*_g = \Delta F_{\text{solv}} + \Delta F^*_s - \Delta F^*_{\text{solv}} \qquad (3)$$

can be expressed as in equation 4. In equation 4,

$$k_g = k_s\, e^{-\Delta F_{\text{solv}}/RT}\, e^{+\Delta F^*_{\text{solv}}/RT} \qquad (4)$$

k_g is the specific rate constant for the reaction in the gas phase and is taken as the "intrinsic" specific rate constant in the absence of solvation effects. Although in principle it is accessible to measurement, in practice it is almost always inaccessible. The specific rate constant of the reaction in solution, k_s, and the free energy of solvation of the reactants, ΔF_{solv}, are both experimentally accessible. The free energy of solvation of the critical complex, ΔF^*_{solv}, is in principle inaccessible to direct experimental measurement. In general, then, equation 4 contains two unknowns, k_g and ΔF^*_{solv}, neither of which can be evaluated independently. However, equation 4 is still useful as a formal representation of the interdependence of the specific rate constant in solution, the "intrinsic" specific rate constant and solvation effects.

If one is interested in the effect of structure or of medium upon the rate of a reaction, one is interested, not in absolute rates, but in relative rates. The obvious extension of equation 4 to represent relative "intrinsic" rates is equation 5, where the primed symbols refer to the same same type of reaction as the unprimed symbols, but to one in which the structure of a reactant or the identity of the medium has been changed.

$$(k'_g/k_g) = (k'_s/k_s)\, e^{-(\Delta F'_{\text{solv}} - \Delta F_{\text{solv}})/RT}\, e^{+(\Delta F^{*\prime}_{\text{solv}} - \Delta F^*_{\text{solv}})/RT} \qquad (5)$$

Equation 5 is basic to our studies of solvation effects and relative rates, the ratio k'_g/k_g being taken as the ratio of "intrinsic" specific rate constants in the absence of solvation effects.

The application of equation 5 to relative rates involving the reaction of the same reactants in two different media is straightforward. Since the reactants and the critical complex are the same for both media, the identities of the gas-phase standard states are immaterial, since gas-phase free energies will cancel in the differences $(\Delta F'_{\text{solv}} - \Delta F_{\text{solv}})$ and $(\Delta F^{*\prime}_{\text{solv}} - \Delta F^*_{\text{solv}})$. These differences then reduce to the changes in free energies associated with the transfer of the appropriate species from their standard states in the unprimed medium to their standard states in the primed medium. Standard states in the two media are conveniently defined by the concentration units employed in the kinetic measurements. Further, since the gas-phase reaction is the same for both media, the ratio k'_g/k_g is unity. Thus, equation 5 simplifies to equation 6. In functional terms, equation 6 predicts that k_s' will tend to be larger than k_s if the

$$k'_s = k_s\, e^{+(\Delta F'_{\text{solv}} - \Delta F_{\text{solv}})/RT}\, e^{-(\Delta F^{*\prime}_{\text{solv}} - \Delta F^*_{\text{solv}})/RT} \qquad (6)$$

standard free energies of the reactants are greater in the primed than in the unprimed medium and if the standard free energy of the critical complex is greater in the unprimed than in the primed medium. If the identities of the reactants are known and if sufficient thermodynamic data on the reactants are available, equation 6 can be used to calculate the standard free energy associated with the transfer of the critical complex between the two media. These conditions are probably satisfied in studies of the unimolecular solvolyses of *t*-butyl chloride in a variety of media,[6,7] and of *t*-butyl bromide in aqueous ethanol.[1] From these studies and other less definitive work,[1,8] it is clear that for relative rates involving the reaction of the same reactants in two different media, solvation effects are of importance *both* in the ground states and in the transition states.

The application of Equation 5 to relative rates involving reactants of different structure in the same medium is ambiguous. However, in view of the theoretical importance attached to interpretation of the effect of structure upon the rate of a type reaction, the application is worth making.

The first difficulty involves the choice of standard states. There seems to be no ambiguity about choosing, as the standard states in solution, hypo-

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(5) The procedure is analogous to that employed for the formulation of equilibrium constants and standard free energies of reaction for different standard states; see, for instance, A. A. Noyes and M. S. Sherrill, "A Course of Study in Chemical Principles," The Macmillan Co., New York, N. Y., 1938, p. 294.

(6) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

(7) A. R. Olson and R. S. Halford, *ibid.*, **59**, 2644 (1937).

(8) M. L. Bird, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 255 (1943).

TABLE I

KINETIC, THERMODYNAMIC AND DERIVED DATA FOR SOME BENZYL CHLORIDES IN METHANOL AT 25.06°

Chloride	$10^7 k_s$, sec.$^{-1}$	p_0, mm.	H, mm./mole/kg. solvent	ΔF_{solv} cal./mole	k'_s/k_s[a]	k'_g/k_g[a]
p-Methylbenzyl	3.06 ± 0.01	0.184 ± 0.002	0.19 ± 0.01	+ 17 ± 30	1	1
Benzyl	0.663 ± .004	.88 ± .01	.43 ± .02	−420 ± 40	0.217	0.46 − 0.102
p-*t*-Butylbenzyl	2.73 ± .03	.017 ± .001	.026 ± .002	+250 ± 50	0.892	1.30 − 0.61

[a] Relative to values for *p*-methylbenzyl chloride.

thetical unit concentrations in the concentration dimensions employed in the kinetic measurements. For standard states in the gas phase, unit fugacities (hypothetical unit pressures in atmospheres) are commonly employed. This convention apparently derives from the fact that gaseous reactions are usually studied with pressure as the concentration dimension, in which case unit fugacities are the "natural" standard states. In the application of equation 5, however, unit fugacities are inappropriate as standard states, for then solvation energies as defined in Fig. 1 vary with molecular weight, generally becoming more negative as molecular weight increases and volatility decreases. Better standard states for our purposes are the fugacities of the vapors in equilibrium with the pure substances. With these standard states, a solvation energy defined as in Fig. 1 becomes (assuming ideal gas behavior) $2.303\, RT \log (p/p_0)$ where p_0 is the saturation vapor pressure of the pure substance and p is its partial pressure over the hypothetical unit concentration solution. For all liquid substances which form ideal solutions (obey Raoult's law at all concentrations) solvation energies are then identical and equal to $2.303\, RT \log X$ where X is the mole fraction of the substances in the hypothetical unit concentration solutions. In our application of equation 5, we employ as standard states in solution the hypothetical 1 molal solutions,[9] and as standard states in the gas phase the saturation vapor pressures of the pure substances. It should be noted that with this convention, ΔF^*_g is the standard free energy change associated with the transfer of reactants from their pure liquid states to the pure liquid state of the critical complex. The value of k_g defined by this ΔF^*_g will not, in general, coincide with any gas-phase specific rate constant that might be measured experimentally.

The second difficulty with the application of equation 5 to the relative rates of reactants with different structures is the fact that, in general, both k'_g/k_g and $(\Delta F^{*\prime}_{solv} - \Delta F^*_{solv})$ are unknown. If the configurations of the critical complexes and the interactions between them and the solvent can be estimated, equation 5 can be used to calculate relative "intrinsic" specific rate constants. Alternatively, the ratio k'_g/k_g might actually be established experimentally, in which case, equation 5 can be used to calculate the difference in solvation energies of the two critical complexes. Our use of equation 5, however, is strictly empirical. We use the derived values $(k'_s/k_s)e^{-(\Delta F'_{solv} - \Delta F_{solv})/RT}$ and $k'_s/(k_s)e^{+(\Delta F'_{solv} - \Delta F_{solv})/RT}$ as limits within which the ratio k'_g/k_g most probably lies. The true value of k'_g/k_g may actually lie outside these limits depending upon the sign and magnitude of the difference $(\Delta F^{*\prime}_{solv} - \Delta F^*_{solv})$. In the absence of information on this difference, however, our procedure offers a reasonable measure of the extent to which differential solvation effects limit the use of the ratio k'_s/k_s as a measure of the ratio of "intrinsic" specific rate constants, k'_g/k_g. If the limits as defined above include unity, we doubt that any meaningful conclusion can be drawn as to the effect of the structural feature being tested upon the "intrinsic" rate of reaction.

In the present study we apply equation 5 to an investigation of the effect of structure upon the solvolysis reactions of benzyl chlorides in methanol at 25.06°. Many reactions of benzyl compounds follow the Baker–Nathan sequence in which the order of reactivity is *p*-methyl > *p*-ethyl > *p*-isopropyl > *p*-*t*-butyl. This sequence was originally,[10] and still is commonly,[11] associated with C–H hyperconjugation. Hyperconjugation is an inherent structural effect which should persist in relative "intrinsic" rate constants as defined by equation 5. It is our purpose to apply the procedure described in the preceding paragraph to the solvolysis reactions of benzyl chlorides in methanol to test whether or not relative specific rate constants obtained in this solution can be used with any assurance as a measure of relative "intrinsic" specific rate constants.

Results

We have studied, from the viewpoint outlined in the Introduction, benzyl chloride, *p*-methylbenzyl chloride and *p*-*t*-butylbenzyl chloride in methanol at 25.06°. Specific first-order rate constants, k_s, for the development of acid from these reactants were determined and are recorded in Table I. As expected, the rate constant for benzyl chloride is lower than those for the *p*-alkylbenzyl chlorides which are in the Baker–Nathan sequence. In fact, the difference in rate constants for *p*-methyl- and *p*-*t*-butylbenzyl chlorides is insignificant, but it is of the order of magnitude usually observed and attributed to differential C–H hyperconjugation.[12]

By application of the dynamic vapor pressure technique and use of ultraviolet spectroscopic analysis, vapor pressures, p_0, of the pure benzyl chlorides and their Henry's law constants, H, in solution were established. Details of the procedures are given in the Experimental section; the results are recorded in Table I. As expected, both p_0 and H decrease as the molecular weight of the substrate increases. However, the decrease in p_0 is more rapid than the decrease in H; as a result, the free

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(9) Molality is used instead of molarity to make hypothetical unit concentration of constant mole fraction regardless of the molecular weight of the solute.

(10) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(11) Conference on Hyperconjugation, Indiana University, June 2–4, 1958; *Tetrahedron*, **5**, 105 (1959).

(12) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1840 (1935).

energies of solvation, ΔF_{solv} (defined as the free energy change of the transformation, pure substrate → hypothetical 1 molal solution), become more positive as molecular weight increases. It is interesting to note that, judged from the effect on ΔF_{solv}, the substitution of *one* methyl group for the *p*-hydrogen on benzyl chloride is more significant than the substitution of *three* methyl groups for the hydrogens on the *p*-methyl group of *p*-methylbenzyl chloride.

Relative specific rate constants also are included in Table I. The relative specific rate constants in solution, $k'_{\mathrm{s}}/k_{\mathrm{s}}$ indicate that the effect of structure on reactivity in solution is in the order *p*-hydrogen < *p*-*t*-butyl < *p*-methyl. As noted in the Introduction, however, differential solvation effects make ambiguous the use of relative specific rate constants in solution as a measure of the effect of structure upon the "intrinsic" rate of reaction. The magnitude of the ambiguity is defined by the magnitude of the differential solvation effects. Thus, the relative "intrinsic" specific rate constants, $k'_{\mathrm{g}}/k_{\mathrm{g}}$, are recorded in Table I as lying between limits as defined in the Introduction and as calculated in the Experimental. It is seen that $k'_{\mathrm{g}}/k_{\mathrm{g}}$ for benzyl chloride relative to *p*-methylbenzyl chloride lies in a range significantly lower than unity. Hence it seems safe to conclude that the effect of structure upon the "intrinsic" rate of reaction lies in the order *p*-hydrogen < *p*-methyl. The ratio $k'_{\mathrm{g}}/k_{\mathrm{g}}$ for *p*-*t*-butylbenzyl chloride relative to *p*-methylbenzyl chloride lies over a range including unity. Hence we doubt that any meaningful conclusion can be drawn about the effect on the "intrinsic" rate of reaction of the substitution of a *p*-*t*-butyl group for a *p*-methyl group.

An alternative way of emphasizing the ambiguity in relative rates introduced by differential solvation effects is in terms of standard free energy differences. For benzyl chloride relative to *p*-methylbenzyl chloride, the difference in standard free energies of activation is +906 cal./mole, and in solvation energies, −437 cal./mole. For *p*-*t*-butylbenzyl chloride relative to *p*-methylbenzyl chloride, the difference in standard free energies of activation is +68 cal./mole, and in solvation energies, +233 cal./mole. From these values it is apparent that the differential solvation effects in the ground states are of the same magnitude as the differential kinetic effects. It should be noted that in the absence of differential solvation effects in the ground states, the ratio of the specific rate constant for *p*-*t*-butylbenzyl chloride relative to that for *p*-methylbenzyl chloride would be less than that actually observed; that is, the Baker–Nathan sequence would be magnified. However, differential solvation effects in the ground states may be cancelled, magnified or reversed by the (inaccessible) differential solvation effects in the transition states. Naively, one might expect differential solvation energies to be larger in the transition states than in the ground states, since the absolute magnitudes of solvation energies in the transition states of ion-producing reactions are larger than those in the ground states. However, there is no way to assess this expectation nor even to predict the signs of differential solvation energies in the transition states.

On the basis of our analysis, we doubt that the Baker–Nathan sequence of reactivity in solution, as observed in this work, can be taken as a reliable indication of "intrinsic" reactivity in the absence of solvation effects. In view of the relative magnitudes of the solvation and kinetic effects observed, we believe that there is much merit in the suggestion[13] that the Baker–Nathan sequence is associated with differential solvation rather than differential C–H hyperconjugation.

Our analysis of solvation effects and the effect of structure upon reactivity is, admittedly, somewhat arbitrary. However, it seems to us to be a rational approach to a difficult problem and it does provide a method for estimating the uncertainty involved in the use of relative rates in solution as a measure of relative "intrinsic" reactivity. Whether or not the analysis is useful depends upon the test of experience and we are engaged in accumulating this experience by extending the analysis to other systems.

Experimental[14]

Materials.—Methanol was Baker and Adamson absolute methanol which was distilled through a 100-plate Stedman column in 3-l. batches just prior to use, and which contained, by Karl Fischer titration, *ca.* 0.01% by wt. of water.

Benzyl chloride was commercial material which was redistilled in a 500 × 15 mm. Heli-Pak column and had b.p. 70° (17 mm.) and $n^{20}\mathrm{D}$ 1.5392 (lit. b.p. 66° (13.5 mm.)[15] and $n^{20}\mathrm{D}$ 1.5392[16]).

***p*-Methylbenzyl chloride**, b.p. 76° (9.5 mm.) and $n^{25}\mathrm{D}$ 1.5320 (lit. b.p. 78° (11 mm.)[15] and $n^{25}\mathrm{D}$ 1.5320[17]), was obtained in 71% yield by the reaction of *p*-methylbenzyl alcohol (185 g.) and concd. hydrochloric acid (1.5 l.) at room temperature for 12 hours. The product was isolated from the two-phase reaction mixture, dried over Drierite, sparged with dry nitrogen gas to remove gaseous hydrochloric acid, and distilled through a 500 × 15 mm. Heli-Pak column.[18] The required ***p*-methylbenzyl alcohol**, m.p. 58–59° (lit.[15] m.p. 59°), was obtained in 75% yield by the reduction of methyl *p*-toluate (150 g., m.p. 33.5–34.0°) with lithium aluminum hydride (29 g.) in ether (1500 ml.).

***p*-*t*-Butylbenzyl chloride**, b.p. 108° (9.5 mm.) and $n^{25}\mathrm{D}$ 1.5196 (lit.[19] b.p. 88–89° (3 mm.) and $n^{24}\mathrm{D}$ 1.5194), was obtained in 55% yield from the addition of *p*-*t*-butylbenzyl alcohol (277 g.) to purified thionyl chloride (279 g.) over a period of 6 hr. at room temp. Crude product was isolated from the reaction mixture by rapid distillation through a short column at 3 mm.; final purification was by fractionation through a 500 × 15 mm. Heli-Pak column. The required ***p*-*t*-butylbenzyl alcohol**,[20] b.p. 120° (6.5 mm.) and $n^{25}\mathrm{D}$ 1.5142–1.5150, **phenylurethan** m.p. 63.5–64.5° (lit.[20] m.p. 62.7–63.4°) was prepared in 87% yield by the reduction of *p*-*t*-butylbenzoic acid (220 g., m.p. 165–166°) with lithium aluminum hydride (47 g.) in ether (2500 ml.).

Vapor Pressure Measurements.—The dynamic vapor pressure method was employed much as described by Grunwald.[21] A schematic representation of the vapor train is

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(13) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, *Tetrahedron*, **5**, 194 (1959), and earlier papers by W. M. Schubert.

(14) Melting points are corrected; boiling points, uncorrected. Temperatures of the constant temperature baths were determined with an NBS calibrated thermometer.

(15) J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 850 (1956).

(16) E. Borello and D. Pepori, *Ann. chim.* (*Rome*), **45**, 449 (1955); *C. A.*, **50**, 205b (1956).

(17) A. C. Farthing, *J. Chem. Soc.*, 3261 (1953).

(18) This method of preparation of benzyl chlorides is superior to that employing thionyl chloride as described below, both with regard to yields and to ease of operation.

(19) E. E. Royals and R. N. Prasad, This Journal, **77**, 1696 (1955).

(20) I. Wender, H. Greenfield, S. Metlin and M. Orchin, *ibid.*, **74**, 4079 (1952).

(21) A. L. Bacarella, A. Finch and E. Grunwald, *J. Phys. Chem.*, **60**, 573 (1956).

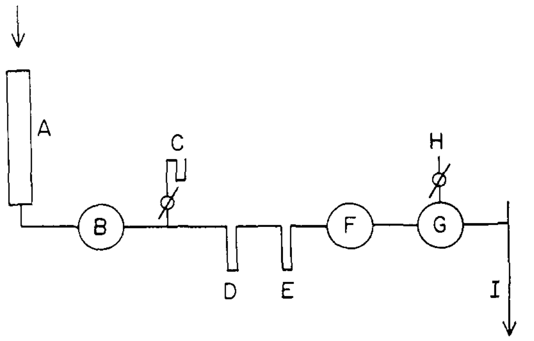

Fig. 2.—Schematic representation of the vapor train used in the vapor pressure measurements: A, drying tower; B, saturator; C, differential manometer; D, condensate trap; E, safety trap; F, wet test meter; G, ballast bottle, H, needle valve; I, water aspirator.

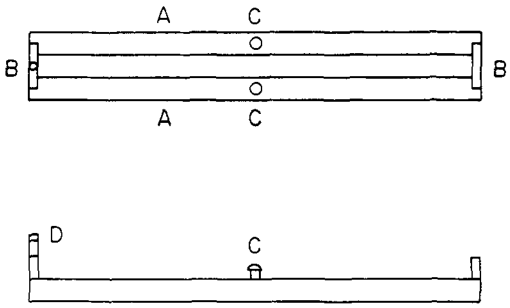

Fig. 3.—A saturator unit: A, saturator tubes (400 × 20 mm.); B, connector tubes (10 mm.); C, 18/9 ball joints; D, 14/35 standard taper female joint with plug.

shown in Fig. 2. The drying tower, A, contained a mixture of Drierite and Ascarite to remove water and carbon dioxide from the air which was used as the entraining gas. The saturator, B, consisted of 5 saturator units, each unit as illustrated in Fig. 3, connected in series through the ball joints by U-tubes and integrated into the vapor train *via* the ball joints at each end of the series. The differential manometer, C, recorded the pressure differential between the saturator and the atmosphere. The traps D and E were detachable and were cooled in a Dry Ice–50:50 chloroform–carbon tetrachloride slush. The wet test meter, F, was a Precision Scientific Co. instrument with a 3-l. cycle and a 3,000-l. recording capacity and was rated at 0.1% accuracy. The vapor chamber of the wet test meter was fitted with a thermometer and a differential manometer, and had water as the hydraulic fluid. Mass flow was induced by the water aspirator, I, the desired (and steady) flow rate being achieved by adjustment of the needle valve, H, on the ballast bottle, G. The line between A and B and from E to I was of 5/16'' i.d. polyethylene tubing; that from B to E was of 10 mm. i.d. Pyrex tubing and was heated as required between B and D by means of a heating tape to prevent premature condensation. The train from A to E was mounted on a brass frame which fitted on a knife edge in the constant temperature bath and was rocked by a 1/120 h.p. motor at 2 cycles/min. through an angle which could be adjusted and was set so that vapor locks were established at the ends of the saturator units on each half-cycle. All joints were sealed with a minimum amount of Apiezon N stopcock grease. The constant temperature bath was 25.07 ± 0.01°.

A vapor pressure run was made in the following manner. The clean components were assembled on the brass frame which was then placed on stops at the appropriate height in the constant temperature bath so that the saturator units were immersed with only the standard taper joints emergent. The aspirator was turned on, the flow adjusted to the desired rate, and pressure differentials were checked on the differential manometer, C, and that on the wet test meter. (In our work, these pressure differentials were always less than 1 mm. and for purposes of calculations the pressure in the vapor train was taken as atmospheric.) The aspirator was then turned off and the cold bath was raised about the safety trap, E. Liquid was then added, *via* the standard taper joints which were immediately plugged, to each of the first four saturator units, the last unit in the series being kept empty as a splash trap. The volume of liquid added per saturator tube was 50 ml. for solutions and 10 ml. for the pure benzyl chlorides. The brass frame was then lowered onto the knife edge (the saturator now being completely immersed), and rocking was started. The aspirator was turned on and a sufficient quantity of air (*ca.* 6 l.) was drawn through the train to ensure equilibration. The aspirator was turned off and the volume reading and the temperature on the wet test meter and atmospheric pressure were recorded. The cold bath was then raised about the condensate trap, D, the aspirator was turned on, and collection of the condensate was begun. After the appropriate volume of air (12–18 l.) had been passed, the aspirator was turned off and the volume reading and temperature on the wet test meter and atmospheric pressure were again recorded. The condensate trap, D, was removed, stoppered and replaced by another trap. The cycle then was repeated. Two or three condensate samples were collected per run.

Analyses for the benzyl chlorides in the condensates were by ultraviolet spectroscopy on a Beckman DU spectrophotometer. Depending upon the concentrations required, the condensates were either transferred directly to the cuvette or were first rinsed out of the traps and diluted to weight with methanol. Optical densities were measured for the solutions at the appropriate wave lengths and were converted to concentrations by means of calibration curves which were established for each benzyl chloride at each wave length. (Beer's law was obeyed for all compounds at all wave lengths.) The appropriate wave lengths represented spectral maxima in methanol and were, with extinction coefficients [in (moles/kg. of solvent)$^{-1}$ cm.$^{-1}$] in parentheses, as follows: benzyl chloride, 260.0 (172), 254.5 (146) and 218.5 (5,400) mμ; *p*-methylbenzyl chloride, 265.0 (202), 258.5 (229) and 224.0 (7,580) mμ; *p*-*t*-butylbenzyl chloride, 263.0 (234), 255.5 (224) and 224.0 (8,480) mμ. The weight of each condensate sample obtained from solutions of the benzyl chlorides was determined from the difference in weight of the condensate trap before and after removal of the sample as corrected for buoyancy. This weight was effectively equal to the weight of methanol condensed.

Calculations of vapor pressures were made with the assumption of ideal gas behavior. For a given condensate sample, the moles of air, n_a, which had passed through the saturator was calculated from the volume metered by the wet test meter, the temperature of the vapor chamber of the wet test meter and the observed atmospheric pressure corrected for the (saturation) vapor pressure of the hydraulic fluid, water. The temperature of the vapor chamber and atmospheric pressure were taken as averages of the values noted before and after the sample was collected. The moles of methanol, n_m, which had passed through the saturator was given directly by the weight of the condensate sample. The moles of benzyl chloride, n_{RCl}, was calculated from its concentration in the spectrophotometric sample and the weight of the condensate or of the diluted sample. The partial pressure of the benzyl chloride, p, was calculated from the equation, $p = p_a[n_{RCl}/(n_a + n_m)]$, where p_a was the observed atmospheric pressure (in mm.); n_m was, of course, zero for measurements involving the pure benzyl chloride, and the vapor pressure, p_0, obtained therefrom was the saturation vapor pressure of the pure compound. Henry's law constant, H, for the benzyl chloride in solution was calculated from the equation $H = p/C$, where C was the concentration (in moles/kg. of solvent) of the benzyl chloride in the saturator solution. That the H measured was a true Henry's law constant was inferred from its constancy over a range of molal concentrations as follows: for benzyl chloride, 0.001–0.08; for *p*-methylbenzyl chloride, 0.0008–0.1; for *p*-*t*-butylbenzyl chloride, 0.004–0.06. That the vapor pressures measured were saturation values was inferred from the constancies of the H and p_0 values, each of which was established at at least two different flow rates in the range, 3–6 l./hr. As a further check on vapor saturation, the partial pressure of methanol, p_m, was calculated from the equation $p_m = p_a[n_m/(n_m + n_a)]$, for all measurements involving solutions and was found to be 130 ± 1 mm. This value compares well with the most precise reported value of 128 mm.[22] which was obtained by the static method and is expected to be somewhat lower than our value because of association in the methanol vapor. From these and other observations, we conclude that our apparatus yields precise vapor densities at flow rates less than *ca.* 9 l./hr., and that at higher flow rates the difficulty appears to be incomplete vapor condensation rather than incomplete vapor saturation.

The values of p_0 and H obtained in this study are recorded in Table I, along with their average deviations. Each p_0 value represents the average of at least four measurements and each H value the average of at least eleven measurements involving at least two different batches of solvent and at least four different solutions.

Kinetic Measurements.—For a kinetic run, a weighed amount of the benzyl chloride was mixed with a weighed amount of methanol which was contained in a glass-stoppered flask and which had reached temperature equilibrium with the constant temperature bath at 25.05 ± 0.01°. At appropriate time intervals, the appropriate weight of solution was pipetted into five times its volume of acetone and 2 ml. of a 0.1% solution of lacmoid in ethanol was added. The solution was then titrated to the lacmoid end-point with *ca.* 0.005 *N* base which had been standardized against sulfamic acid in the same medium and with the same indicator. The solvent titer was found to be negligible. Six to twelve aliquots were taken in each kinetic run, extending over the range 0–5% reaction with benzyl chloride and 0–25% reaction with the *p*-alkylbenzyl chlorides.

Rate constants were calculated from the equation, $\log[1/(a - x)] = (k_s/2.303)t - C$, where a is the initial concentration of the benzyl chloride as calculated from the weights of reactant and solvent, x is the concentration of acid as determined by titration, t is the time, C is the (undetermined) constant of integration and k_s is the specific first-order rate constant. The rate constant was taken as the slope, multiplied by 2.303, of the best visual straight line drawn through the points in a plot of $\log[1/(a - x)]$ *vs.* t.

The rate constants obtained are recorded in Table I along with their average deviations. Each value is the average from at least four different kinetic runs, half of which were made before, and half after, the vapor pressure measurements, and which involved at least two different batches of solvent. The kinetic solutions were all *ca.* 0.01 molal in the benzyl chlorides except with benzyl chloride itself, for which kinetic runs were made with *ca.* 0.1 molal solutions as well, and for which the rate constant was found to be independent of concentration. For each benzyl chloride, two kinetic runs were made in solvent to which sufficient water had been added to make it *ca.* 0.1% by wt. water (10 times the water concn. in the pure solvent). In each case, the specific rate constant was identical with that obtained in the pure solvent.

Calculations.—For each benzyl chloride, the free energy of solvation corresponding to the transfer of 1 mole of pure substance to the hypothetical 1 molal solution was calculated from the equation, $\Delta F_{\text{solv}} = 2.303\,RT \log H/p_0$. The ratio of "intrinsic" specific rate constants, k'_g/k_g, was taken as lying between the limits defined by the expressions, $(k'_s/k_s)\cdot e^{-(\Delta F'_{\text{solv}} - \Delta F_{\text{solv}})/RT}$ and $(k'_s/k_s)e^{+(\Delta F'_{\text{solv}} - \Delta F_{\text{solv}})/RT}$ which simplify to $(k'_s/k_s)(Hp'_0/H'p_0)$ and $(k'_s/k_s)(H'p_0/Hp'_0)$. The values obtained are recorded in Table I.

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[CONTRIBUTION FROM THE DOW CHEMICAL CO., EASTERN RESEARCH LABORATORY]

Electronic Interactions in Phenyl Acetates and Acetanilides[1]

BY H. H. FREEDMAN

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The relative importance of an inductive *vs.* a resonance mechanism for the high carbonyl absorption frequency of phenyl acetate and acetanilide has been investigated. A study of the C=O frequency shifts in their *m*- and *p*-substituted derivatives clearly shows that the inductive mechanism is responsible for the frequency shift in phenyl acetate, but a resonance mechanism is more appropriate in the acetanilides. This is supported by a study of their respective Stuart–Briegleb molecular models which, on the basis of steric inhibition of resonance due to lack of coplanarity within the molecule, indicates that a resonance mechanism is relatively unimportant in phenyl acetate.

It has been long known that the introduction of an unsaturated group on the alcohol moiety of an ester, as in phenyl or vinyl acetate, causes a shift to higher frequency in the ester carbonyl stretching band.[2,3] Thus Hartwell[4] found that methyl, vinyl and phenyl acetate absorb at 1747, 1762 and 1766 cm.$^{-1}$ in the liquid state and Jones[5] reported a carbonyl frequency increase of 30 cm.$^{-1}$ in steroid acetate esters when cycloalkyl is replaced by phenyl. A similar though lesser displacement is observed with amides, and this was first reported by Richards and Thompson[6] who noted that the carbonyl band of acetanilide was at a distinctly higher frequency than that of N-alkyl substituted amides.

Two explanations have been offered for these carbonyl shifts. The simpler of these maintains that the high frequency of vinyl acetate is due to the replacement of the electropositive alkyl group by the electronegative vinyl, the latter "increasing the electron-attracting power of the oxygen atom in the —O—CH=CH$_2$ group, thus diminishing the ionic character of the carbonyl link."[4] Rasmussen and Brattain[7] support this hypothesis and point out that 1,1-diacetoxypropane, $CH_3CH_2CH(OCOCH_3)_2$, also exhibits its ester band at shorter wave lengths than normal (1761 cm.$^{-1}$) and that this must be due to the mutual effect of the negative acetoxy groups. Presumably, then, this effect is directly analogous to that of α-halogenated ketones whose enhanced C=O frequencies have been directly attributed to the inductive (and field) effect of the electronegative halogen.[8] For

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[1] Presented in part at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1958.

[2] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 182.

[3] R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, Chap. IV, p. 483.

[4] J. H. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

[5] R. N. Jones, *et al.*, THIS JOURNAL, **74**, 2820 (1952).

[6] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

[7] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

[8] Reference 3, p. 474.