ligible. Positive ions are expected to remain in the vicinity of the discharge (upper) electrode due to its high negative field. Excited species are apparently quenched near the discharge electrode since the addition of a quenching gas (*i.e.*, CO_2) increases rather than decreases the yield in a number of reactions. Furthermore, the gas flow in the reaction vessel is such that the test vapors are carried in a direction away from the discharge electrode so that there should be little contact between the test material and positive ions and excited species.

In general, photochemical reactions have very low efficiency, thus requiring intense light sources, reflection, etc., for measurable reactions to occur. The discharge in our apparatus is a soft, diffuse glow and maintained rarely in excess of 2 hr. Consequently, the effect of photons on these reactions is considered negligible.

It was not determined whether the reactions occur in the gas phase or in the liquid phase. However, some evidence indicates that the reactions occur in the gas phase. If the reactions occur in the liquid phase, then the H value would be dependent upon the time the electrons travel through the liquid phase and this time would depend on the liquid phase thickness. Thus the H value would be a function of the sample weight. It was found, however, that the H values did not vary with the weight of reactant. This then indicates that the reactions occur in the gas phase.

Conclusions

A corona discharge is a simple, inexpensive means for the generation of near thermal energy electrons. Although the electrons are not monoenergetic, large changes in their energy can be effected through use of a polyatomic energy-moderating gas. Experiments with this discharge cell indicate that both dissociative and nondissociative electron capture can be observed. Dissociative capture was confirmed for chlorobenzene and benzyl chloride, while benzaldehyde, diethyl maleate, and *cis*-stilbene were shown to attach electrons in a nondissociative manner. Of particular significance is the fact that the products of these reactions are actually recovered and characterized by gas chromatography–mass spectrometry. This technique should find application for both organic syntheses and investigation of the role of free electrons in biological systems.[8]

Acknowledgment. Support of this research by Grant No. AP 00308-06 from the Consumer Protection and Environmental Health Service, Public Health Service, and Contract No. AT-(40-1)-3541 from the Atomic Energy Commission is gratefully acknowledged.

Heats of Transfer of β-Dicarbonyl Compounds from Carbon Tetrachloride to Sulfuric Acid

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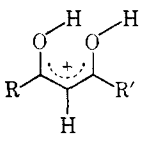
Abstract: The relative heats of transfer from carbon tetrachloride to concentrated sulfuric acid for a series of compounds containing β-carbonyl groups have been measured. A large Baker–Nathan effect has been observed on the heats of transfer of substituted β-diketones. The destabilization of protonated carbonyl compounds in H_2SO_4 when methyl is replaced by phenyl has been observed. It is suggested that the size of the organic ion may play a significant role in the substituent effects observed in this system.

The interaction of compounds containing β-carbonyl groups with Lewis and Brønsted acids has been of continuing interest. Most attention has been focused on the complexes of β-dicarbonyl compounds with various metals.[1] However quite recently Olah and Brouwer have independently reported nmr studies of mono- and diprotonated β-diketones,[2–4] alkyl acetoacetate derivatives,[2] and malonic acid derivatives.[2] Other nmr studies of protonated β-dicarbonyl compounds have been made by Deno[5] and Olah.[6] These studies indicate that the compounds are protonated cleanly, no products other than the protonated species being detected by nmr. Studies in these laboratories confirm that these reactions are completely clean within our limits of detection. In addition, a thorough study of the protonation of acetylacetone in aqueous sulfuric acid using acidity function techniques has been reported.[7]

The observation by Brouwer[2] that the ion formed by protonation of a β-dicarbonyl compound (RC(=O)-CH$_2$C(=O)R′) has the structure I when R is alkyl or aryl and II when R and R′ are alkoxyl is particularly interesting. In order to compare the stabilities of I and



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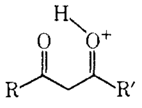

II

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(1) J. P. Fackler, Jr., *Advan. Chem. Ser.*, No. 62, 580 (1967).

(2) D. M. Brouwer, *Recl. Trav. Chem. Pays-Bas*, 87, 225 (1968).

(3) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, 90, 4672 (1968).

(4) D. M. Brouwer, *Chem. Commun.*, 515 (1967).

(5) N. C. Deno, H. G. Richey, N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, *J. Amer. Chem. Soc.*, 85, 2991 (1963).

(6) G. A. Olah and C. U. Pittman, *ibid.*, 88, 3310 (1966).

(7) W. Walisch and H. G. Hahn, *Chem. Ber.*, 94, 790 (1961).

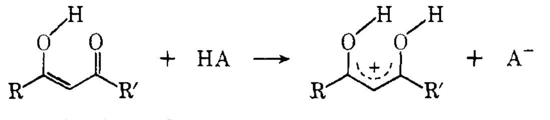
Table I. Relative Heats of Protonation for β-Diketones and Model Compounds[a]

No.	Compd	$\Delta\overline{H}_{sCCl_4}$,[b] kcal/mol	ΔH_T, H_2SO_4, kcal/mol	ΔH_T, HSO_3F, kcal/mol
1	$CH_3COH{=}CHC({=}O)CH_3$	+0.80 ± 0.05	−17.0 ± 0.2	−22.5 ± 0.4
2	$EtCOH{=}CHC({=}O)Et$	+0.51 ± 0.09	−16.4 ± 0.2	
3	*i*-PrCOH=CHC(=O)-*i*-Pr	+0.38 ± 0.08	−15.9 ± 0.1	
4	*t*-BuCOH=CHC(=O)-*t*-Bu	+0.17 ± 0.03	−12.9 ± 0.2	−18.7 ± 0.4
5	$PhCOH{=}CHC({=}O)CH_3$	+0.35 ± 0.14	−15.40 ± 0.21	−22.2 ± 0.2
6	$PhCOH{=}CHC({=}O)Ph$	+5.95 ± 0.30	−11.19 ± 0.50	−18.6 ± 0.4
7	PhC(=O)—CHCOOEt	+1.32 ± 0.05		−20.8 ± 0.1
8	$CH_3OCH{=}CHC({=}O)CH_3$	+1.15 ± 0.02	−19.8 ± 0.2	−25.8 ± 0.9
9	$CH_3C({=}O)OCH_2C({=}O)CH_3$	+2.35 ± 0.09	−14.0 ± 0.2	
10	$CH_3C({=}O)OEt$	+0.05 ± 0.02	−12.0 ± 0.1	
11	$PhC({=}O)OEt$	+0.28 ± 0.04	−8.97 ± 0.16	
12	$CH_3C({=}O)CH_3$	+0.79 ± 0.02	−12.3 ± 0.1	−19.1 ± 0.1
13	$PhCH_2C({=}O)CH_3$	+1.17 ± 0.04	−10.27 ± 0.09	
14	$CH_2(COOMe)_2$	+1.65 ± 0.05	−12.4 ± 0.4	−19.6 ± 0.1
15	$PhCH(COOEt)_2$	+0.89 ± 0.05	−10.36 ± 0.20	−17.3 ± 0.3
16	$Me_2C(COOEt)_2$	+0.17 ± 0.03	−12.8 ± 0.6	−19.5 ± 0.3

[a] In 99.5% H_2SO_4 and HSO_3F at 25°. [b] For the neat liquid mixture of keto and enol forms.

II with respect to each other and with respect to other protonated compounds, we have measured the heats of transfer of a variety of compounds containing β-carbonyl groups from carbon tetrachloride to sulfuric acid. All of the compounds studied are monoprotonated in the concentrated sulfuric acid used. Substituent effects on the stability of these ions are also of interest.

Since many of the compounds of interest exist as a mixture of the keto and enol forms,[8] a choice of a standard state must be made. The fact that malonic acid derivatives exist essentially completely in the keto form[9] makes that the most desirable standard state. However several of the β-diketones exist completely in the enol form[10] and all of the heats of isomerization necessary to calculate the heat of transfer of the keto form are not known. Because of this, the heats of transfer of the β-diketones reported in Table I refer to the enol as standard state, *i.e.*, correspond to the reaction shown below. Data for malonic acid derivatives refer to the keto form as standard state.



The use of carbon tetrachloride as an inert solvent has been discussed previously.[11,12] Several of the β-diketones exist as a mixture of the keto and enol forms in carbon tetrachloride. The enthalpy cycle shown is used to correct the observed values to the enol form standard state. Here E and K denote the enol and keto forms, respectively, and X is the fraction of the compound existing as the enol in carbon tetrachloride. The observed heat of transfer (ΔH_{obsd}) of the compound from carbon tetrachloride to the acid is

$$\Delta H_{obsd} = X\Delta H_{T,E} + (1 - X)\Delta H_{T,K} \qquad (1)$$

$$\begin{tikzcd}
X\mathrm{E}_{\mathrm{CCl}_4} \arrow[r, "\Delta H_{\mathrm{E-K}}"] \arrow[d, "\mathrm{HA}"', "\Delta H_{\mathrm{T,E}}"] & (1-X)K_{\mathrm{CCl}_4} \arrow[dl, "\mathrm{HA}", "\Delta H_{\mathrm{T,K}}"'] \\
\mathrm{EH}^+ + \mathrm{A}^- &
\end{tikzcd}$$

This value is obtained experimentally by subtracting the heat of solution of the compound in carbon tetrachloride from the heat given off when the compound is dissolved in (and reacts with) the acid, *i.e.*

$$\Delta H_{obsd} = \Delta H_{acid} - \Delta\overline{H}_{sCCl_4}$$

From the enthalpy cyclic shown above, $\Delta H_{T,E} = \Delta H_{E-K} + \Delta H_{T,K}$. Combining this with eq 1 gives

$$\Delta H_{T,E} = \Delta H_{obsd} + (1 - X)\Delta H_{E-K} \qquad (2)$$

Since ΔH_{obsd} is easily measured and ΔH_{E-K} can be obtained or estimated from data in the literature $\Delta H_{T,E}$, the heat of transfer of the enol, can be obtained easily. Both compounds **5** and **6** in Table I are completely enolized in carbon tetrachloride as shown by their nmr spectra. For compounds **2**, **3**, and **4** the amount of enol in the neat liquids and the heats of enolization in the neat liquids are known.[9] The heats of enolization in carbon tetrachloride were calculated for these compounds by assuming the solvent dependence of the equilibrium constant for enolization was the same for these compounds as for acetylacetone and that the heat of enolization was the same in carbon tetrachloride as in the neat liquid. That these are reasonable assumptions is indicated by the similarity in solvent dependence of the equilibrium constants of several compounds and the very small solvent dependence of the heat of enolization of acetylacetone observed by Powling and Bernstein.[13] In any case, any error introduced by these assumptions would not be more than 0.1 or 0.2 kcal/mol. The data of Grossmann[14] were used to correct the values for ethyl acetoacetate. Sufficient data are available for acetyacetone (**1**)[13] to enable this calculation to be made exactly. The correction made was 0.3 kcal/mol for compounds **1–4** while that for compound **7** was 0.9 kcal/mol.

The most striking feature of the data presented in Table I is the very large Baker–Nathan effect observed, the di-*t*-butyl ion (from compound **4**) being less stable than the dimethyl ion (from compound **1**) by 4.1 kcal/

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(8) G. K. Schweitzer and E. W. Benson, *J. Chem. Eng. Data*, 13, 452 (1968).

(9) J. Calmon, *C. R. Acad. Sci., Ser. C*, 268, 1435 (1969).

(10) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, 86, 2105 (1964).

(11) E. M. Arnett and J. W. Larsen in "Carbonium Ions," Vol. 1, G. A. Olah and P. Von R. Schleyer, Ed., Wiley, New York, N. Y., 1968.

(12) E. M. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 1438 (1969).

(13) J. Powling and H. J. Bernstein, *ibid.*, 73, 4353 (1951).

(14) P. Grossmann, *Z. Phys. Chem.*, 109, 305 (1924).

mol. Baker–Nathan effects of this magnitude have only been observed twice previously.[12,15] Previous arguments used to rationalize this effect have been based on predominant C–H hyperconjugation,[16,17] steric hindrance of specific solvation,[18] steric hindrance to bond shortening,[19] and hydrogen bonding involving the hydrogens of the alkyl substituent.[20,21] These arguments can be applied to the system under consideration here and used to rationalize these data.

The ions under consideration vary greatly in size, and it may be possible that ion size alone can have sufficient influence on interactions with the solvent to rationalize the observed effect. The effect of solute size on solvent–solute interactions can be calculated using a variety of simple thermodynamic models. While such calculations are not capable of distinguishing unequivocally between internal energy effects and solvent–solute interactions as explanations of the Baker–Nathan order observed here, they can indicate whether an explanation based on solvent–solute interactions is a real possibility. It will become apparent that, in the absence of other effects, the Baker–Nathan order is predicted by a simple evaluation of the solute–solvent interactions in this system. Moreover, the predicted substituent effects are of the same order of magnitude as the observed effects. To facilitate an examination of the possible effects of differing molecular diameters, it will be assumed that differences in inductive and resonance effects in the series methyl, ethyl, isopropyl, and *t*-butyl are negligible, that ions 1–4 have essentially the same stability in the gas phase.

There are two ways in which size will influence the stability of an ion in solution. One is due to the different cohesive energy densities[22] of carbon tetrachloride and sulfuric acid and the fact that the enthalpies reported here are heats of transfer from carbon tetrachloride to sulfuric acid. The cohesive energy density is given by $\delta = (E/V^1)^{1/2}$, where E is the energy of vaporization at zero pressure and V^1 is the molal volume of the liquid. From the heat of vaporization of sulfuric acid[23] the value of δ for sulfuric acid can be estimated as being about 15 $\mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}$.[24] This is quite high, and much higher than the value for carbon tetrachloride ($\delta = 8.6\ \mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}$).[25] In a somewhat oversimplified view, δ can be regarded as a measure of the energy required to create a cavity in a solvent to contain the solute. Thus transferring a molecule from carbon tetrachloride to sulfuric acid will require energy to create cavities in the acid to contain the solute. The larger the solute molecule the larger the cavity which must be created. The second effect which must be considered is that of ionic size on the electrostatic interaction of the ion with the solvent; the larger the ion, the smaller the enthalpy resulting from its electrostatic interaction with the solvent. Both of these effects are in the same direction and qualitatively predict the observed trend, the destabilization of the larger ions with respect to the smaller. It is expected that the heat of transfer will be given best by the sum of these two processes. The first stage is the transfer of the neutral molecule from carbon tetrachloride to the acid and this is calculated using regular solution theory. The interaction of the protonated species with solvent is then evaluated using the simple sphere in a dielectric model.

To consider these effects in as quantitative a fashion as possible we shall first calculate the enthalpy change due to the different cohesive energy densities of carbon tetrachloride and the acid. Using the previously given values of δ for sulfuric acid and carbon tetrachloride and estimating δ for the diketones from their boiling points,[25,26] it can be calculated that ion **4** should be destabilized with respect to ion **1** by about 2.5 kcal/mol.[27] Friedman[28] has recently used this approach in estimating heats of transfer of several inorganic ions.

Assuming the ion is a sphere immersed in a dielectric continuum,[29] its enthalpy of interaction with the solvent can be calculated.[30] Previous attempts with this model have not always been successful.[31] The relevant equation obtained by taking the temperature derivative of the modified Born equation[31] is

$$\Delta H_{\mathrm{i}}^{\circ} = \frac{-e_{\mathrm{i}}^{2}(1 - 1/\epsilon)}{2(r_{\mathrm{i}} + \Delta)}\left[1 - \frac{T(\partial\epsilon/\partial T)}{\epsilon(\epsilon - 1)} + \frac{T}{r + \Delta}\frac{\partial\Delta}{\partial T}\right]$$

Here ϵ is the dielectric constant of the solvent and Δ is an empirical correction to the ion radius r. For large values of ϵ (for H_2SO_4 $\epsilon = 120$ at 25°)[32] and making the assumption that $\partial\Delta/\partial T = 0$, one obtains $\Delta H_{\mathrm{i}} = -e_{\mathrm{i}}^{2}/2(r_{\mathrm{i}} + \Delta)$. Ignoring the correction factor Δ and using r measured from Dreiding models, it is predicted that ion **4** is 5.8 kcal/mol less stable than ion **1**. However, as seen in Figure 1, a plot of ΔH *vs.* $1/r$ is not a good straight line. The line shown in Figure 1 is that calculated using the sphere in continuum model. While the order of magnitude is correct, both the *t*-butyl and isopropyl substituted ions are more stable than predicted. This model is sufficiently crude so that it does not seem wise to attempt to ascribe any significance to this deviation.

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(15) T. Sorenson, *J. Amer. Chem. Soc.*, **89**, 3782, 3794 (1967).

(16) V. J. Shiner and E. Campaigne, "Conference on Hyperconjugation," Pergamon Press, Elmsford, N. Y., 1959.

(17) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(18) W. A. Sweeney and W. M. Schubert, *J. Amer. Chem. Soc.*, **76**, 4625 (1954); W. M. Schubert, J. M. Craven, R. G. Minton, and R. B. Murphy, "Conference on Hyperconjugation," Pergamon Press, Elmsford, N. Y., 1959.

(19) A. Burawory and E. Spinna, *J. Chem. Soc.*, 3752 (1956).

(20) V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **72**, 1603 (1954).

(21) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 829 (1970).

(22) For a thorough discussion of this quantity, see ref 25.

(23) "International Critical Tables," Vol. V, McGraw-Hill, New York, N. Y., 1963, p 136.

(24) The heat of vaporization of sulfuric acid reported by Luchinskii (G. P. Luchinskii, *Zh. Fiz. Khim.*, **33**, 1275 (1959); *Chem. Abstr.*, **54**, 8263*i* (1960)), leads to a slightly higher value for δ.

(25) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publications, New York, N. Y., 1964.

(26) W. G. Scribner, "Physical Properties of Selected β-Diketones" Technical Research Report ARL-TR-67, Office of Aerospace Research, U. S. Air Force.

(27) The heat of transfer of a solute molecule (C) from solvent A to B is given by $\Delta H_{\mathrm{T}} = V_{\mathrm{c}}(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})(\delta_{\mathrm{A}} + \delta_{\mathrm{B}} - 2\delta_{\mathrm{c}})$. The molar volumes ($V_{\mathrm{c}}$) of the neat liquid diketones were used.

(28) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 3934 (1969).

(29) Arnett has shown that the behavior of carbonium ions in water is consistent with the sphere in continium model (E. M. Arnett and R. D. Bushick, *J. Amer. Chem. Soc.*, **86**, 1564 (1964)), and Szwarc (M. Kalfoglou and M. Szwarc, *J. Phys. Chem.*, **72**, 2233 (1968)) has demonstrated this behavior for carbanium ions in methylene chloride.

(30) W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

(31) R. P. Held and C. M. Criss, *J. Phys. Chem.*, **71**, 2487 (1967).

(32) R. A. Gillespie and E. A. Robinson in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N. Y., 1965.

Combining the results of the transfer of the neutral molecule to sulfuric acid and the calculation of the electrostatic interaction, the *t*-butyl substituted ion is calculated to be 8 kcal/mol less stable than the methyl substituted ion. The results for the diisopropyl ion are of the same order of accuracy while the agreement with experiment is significantly better for the diethyl case.

The purpose of this paper is not to suggest that solvent–solute interactions are the only explanation of the Baker–Nathan order observed here. We do wish to point out that a consideration of solvent–solute interactions predicts the existence of a Baker–Nathan order of the same magnitude as that observed here and that such interactions should be considered.

Our conclusions about the large Baker–Nathan effect observed here can be summarized briefly. (1) It is not possible on the basis of these data to decide between a solvent effect and an electronic substituent effect (hyperconjugation), or one of the effects previously mentioned as the source of the observed Baker–Nathan order. (2) One need not postulate steric hindrance to specific solvation to explain these data using solvent effects. The classical, nonspecific interactions of solvent with ions of different size are sufficient.

The model discussed here rationalizes the very large Baker–Nathan effect observed here on the basis of simple solution thermodynamics. There are other data to which this model can be applied, specifically recent papers by Arnett[12] and Sorensen.[15] Since this model is much too crude to apply to the small Baker–Nathan effects observed in solvolysis reactions, discussion will be limited to the much larger effects found in strong acid systems.

The large Baker–Nathan effect recently observed by Arnett and Larsen[12] can be rationalized using the concepts described above. As they pointed out, the fact that the monoisopropylbenzenium ion is more stable than the 2,4,6-triisopropylbenzenium ion is strong evidence that solvation effects are important. Particularly this indicates that increased substitution (size) can result in a decrease in stability.

Sorensen[15] has also observed a large Baker–Nathan effect in substituted cyclopentenyl cations in sulfuric acid. It is very difficult to explain his data on the basis of differing ionic sizes. Dreiding models indicate that the two equilibrating ions are of about the same size. To explain his data using the models discussed here, one is forced to postulate that one ion (the more stable one) assumes a conformation in solution which is significantly smaller than the other. However, this system is complicated somewhat by steric interactions which are quite difficult to evaluate quantitatively. These data can be rationalized, as Sorensen does, on the basis of hyperconjugation.

A few comments on the application of the two effects discussed above to other systems seem in order. Of particular interest is the consideration of ion size effects on relative stabilities of ions generated from a precursor in a single solvent. Consider first the effect of cohesive energy density (δ). For systems in which the molecule is not transferred from one solvent to another (*e.g.*, the equilibrium protonation of a carbonyl compound or an olefin) to a first approximation the cohesive energy density of the solvent would affect the energy of the process only insofar as the two species (ion and covalent precursor) differed in size. The effect would be probably quite small. However the effect of ionic size on the electrostatic interaction need not be small. For a series of ions of decreasing size, the enthalpy of interaction would increase. When ions of differing sizes are produced in a common solvent, there should result an energy difference between the ions due to the effect of size on the electrostatic interactions between the ion and the solvent. This effect of varying ionic size in alkyl-substituted ions is in the same direction as steric hindance to specific solvation and it will be extremely difficult to distinguish between them.

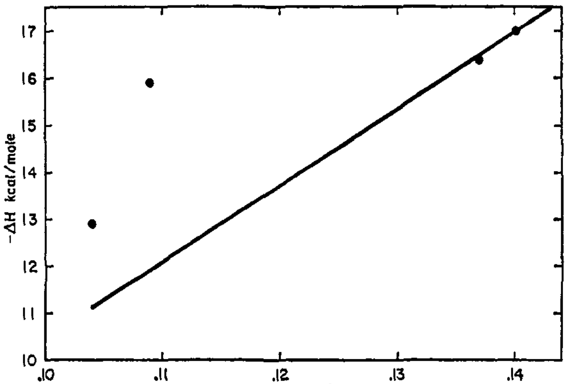

Figure 1. Heat of transfer of some β-diketones ($\Delta H_{\mathrm{T,E}}$) *vs.* $1/r$ where r is the radius of the ion.

It seems impossible on the basis of the limited data now available to unequivocally accept or reject the effects of ionic size as explanations of the heats of transfer discussed here. We wish to suggest only that they are worthy of some consideration. As more data become available we hope to evaluate more rigorously the importance of these effects in systems involving large organic ions. Application of these models to the calculation of relative stabilities of ions using data from the literature as well as further experimental work designed to test these models is in progress.

Another striking substituent effect observed in this system is the destabilization of the ion relative to the starting material when methyl is replaced by phenyl. Increased stabilization by phenyl has been widely observed in solvolysis reactions[33] and more recently in stable carbonium ions.[34] However, the opposite behavior is also widespread. Deno has observed that the 1,3-dimethylcyclopentenyl cation is half-formed from the diene in 35% sulfuric acid while the 1,3-diphenylcyclopentenyl cation requires 50% sulfuric acid for half-formation.[35] Breslow has reported that the diphenylcyclopropenyl and dipropylcyclopropenyl cations are of almost identical stability[36] as measured by acidity function techniques. Analogous substituent effects by phenyl have also been observed on the heats of complexation of ketones with Lewis acids in various solvents[37–39]

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[33] A. Streitwieser, Jr., "Solvoltytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

[34] E. M. Arnett and J. W. Larsen, "Carbonium Ions," Vol. 1, G. A. Olah and P. von R. Schleyer, Ed., Interscience, New York, N. Y., 1968.

[35] N. C. Deno, *Chem. Eng. News*, **42**, 88 (Oct 5, 1964).

[36] R. Beslow and H. Hover, *J. Amer. Chem. Soc.*, 82, 2644 (1960).

[37] C. S. Giam and R. W. Taft, *ibid.*, **89**, 2397 (1967).

[38] M. H. Dilke, D. D. Eley, and M. G. Sheppard, *Trans. Faraday Soc.*, **46**, 261 (1950).

as well as on the heats of protonation of ketones in fluorosulfonic acid.[40] In addition to this effect, the destabilization by phenyl with respect to methyl has been observed in the solvolysis of 1-phenylnorbornyl 2-*exo*-chloride.[41] Also this effect has been reported by Ciabattoni and Nathan[42] who observed a similar substituent effect on the p*K*'s of substituted cyclopropenyl cations in aqueous sulfuric acid and concluded that it must be due to solvation.

The data in Table I show that replacing a methyl group by a phenyl results in a decreased (less exothermic) heat of transfer by about 2–4 kcal/mol *regardless of whether the phenyl is conjugated to the carbonyl group being protonated.* This suggests that some factor other than, or in addition to, a resonance or inductive effect is operating. It is of course possible that two electronic substituent effects may be occurring. The decrease in heat of protonation observed in benzyl substituted carbonyl compounds compared to the methyl substituted compounds may be due to inductive electron withdrawal by the benzyl group. The decrease caused by a phenyl substituent may be due to greater stabilization of the ground state than of the ion by the phenyl group.[39,43,44] However, it is also possible that the observed effect is caused by a large destabilization due to the large size of the phenyl group (solvent effect) superimposed on a smaller stabilization of the ion by resonance. That is, the destabilization due to increased ionic size predicted using the models discussed previously is greater than that observed experimentally. It does not seem possible at this time to decide between these two rationalizations. It should be pointed out that due to steric interference between the *ortho* protons and the hydroxyl hydrogen, the phenyl group may be twisted out of the plane of the allylic π system. However, a recent nmr study of this system indicates that there is appreciable overlap between the phenyl ring and the enol π system.[43]

A comparison between the heats of protonation of the β-diketones and the diesters sheds light on the reason the β-diketones exist as dihydroxyallyl cations while the protonated esters do not enolize.[2] The heat of protonation of dimethylmalonate is the same as the heat of protonation of acetone while phenyldiethylmalonate has the same heat of protonation as phenylacetone. It is quite apparent that in spite of its large size, the protonation of the β-diketone is much more (*ca.* 5 kcal/mol) exothermic than the model ketones. This indicates stabilization due to formation of the dihydroxyallyl cation. The reason the protonated esters do not form the allylic cation must be due to a destabilization of the allylic ion by the alkoxy groups. It was observed long ago by a variety of workers[45] that replacing alkyl groups by alkoxy groups reduced the stability of the enol with respect to the keto form.

Experimental Section

The calorimeter and experimental procedures are similar to those described by Arnett and Larsen.[12] With the exception of those listed below, all compounds were commercially available and were, when necessary, distilled or recrystallized before use. All compounds were dried thoroughly, liquids over 4-Å molecular sieves and solids over P_2O_5 under vacuum. 3,5-Heptanedione and 2,6-dimethyl-3,5-heptanedione were prepared by the procedure of Benson.[46]

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Many helpful discussions with Dr. Mike Pikal and Dr. J. F. Eastham and the comments of Dr. W. M. Schubert are gratefully acknowledged.

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(39) R. C. Paul, S. C. Ahlewalia, and R. Parhash, *Indian J. Chem.*, 6, 469 (1968).

(40) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, 92, 3977 (1970).

(41) H. C. Brown, F. J. Chloupek, and M. Rei, *ibid.*, 86, 1246 (1964), and P. Schleyer and D. C. Kleinfelter, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 43P.

(42) J. Ciabattoni and E. C. Nathan, III, Abstracts of Papers, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(43) D. J. Sardella, D. H. Heinat, and B. L. Shapiro, *J. Org. Chem.*, 34, 2817 (1969).

(44) J. W. Larsen, S. Ewing, and M. Wynn, *Tetrahedron Lett.*, 539 (1970).

(45) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed, Wiley, New York, N. Y., 1949, p 580.

(46) E. W. Benson, Ph.D. Thesis, University of Tennessee, Knoxville, Tenn., 1967.