

Reactivity and Ion Pairing of Alkali β -Ketoenolates

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Abstract: Solutions of alkali and tetrabutylammonium salts of dibenzoyl methane (DBM) and dipivaloylmethane (DPM) in dimethyl sulfoxide (Me₂SO) and tetrahydrofuran (THF) have been examined by a variety of methods to determine the degree of association and the nature of the associated species. Ion-pair dissociation constants were determined for Na⁺, K⁺, Cs⁺, Bu₄N⁺ salts of DBM and DPM in Me₂SO. Conductances of the Li⁺ salt in Me₂SO were too small to allow meaningful analysis. Rate constants for alkylation were determined by a calorimetric technique. For carbon methylation of the dibenzoylmethides with methyl iodide in Me₂SO, second-order rate constants correlate with the conductometrically determined degree of dissociation for the initial concentration of the enolate salt solution, supporting the notion that the free anions are much more reactive than are the ion pairs. Oxygen methylation of the alkali dibenzoylmethides with dimethyl sulfate in Me₂SO was found to occur by two competing mechanisms. The rate-determining step of one mechanism is the formation of a highly reactive dimethylmethoxysulfonium sulfate intermediate, which then attacks both free ions and ion pairs to form the β -keto vinyl methyl ether. The other mechanism is a typical S_N2 reaction between the alkali β -ketoenolate and dimethyl sulfate. This second-order rate constant varies with the degree of dissociation of the initial concentration of the enolate solution implying that the free ions are the reactive species. The ion pairs appear to be unreactive to these alkylations in Me₂SO. In Me₂SO the ¹H and ¹³C NMR spectra showed characteristic chemical shifts which vary inversely with the size of the cation. In the case of the ¹H NMR chemical shifts the δ vs. $1/r$ correlation is linear. More significantly, a cation-sensitive, far-infrared absorption band of the various enolate salts varied as the reciprocal of the alkali cation radius. This implies, not only that the alkali β -ketoenolates are ion paired, but also that they form contact ion pairs. Similarly, Bjerrum-distance calculations from the calculated dissociation constants imply that the alkali and tetrabutylammonium dibenzoylmethides form contact ion pairs. Ultraviolet ($\pi_3 \rightarrow \pi_4^*$) absorptions were somewhat sensitive to solvent changes but were surprisingly independent of cation. Heats of alkylation with methyl fluorosulfonate could not be determined in Me₂SO because of competitive nucleophilic attack by this solvent on the alkylating agent. Thermochemically determined enthalpies of reaction for the methylation of the alkali β -ketoenolates in propylene carbonate (PC) and tetrahydrofuran (THF) provided few surprises. In PC, the enolates were predominately oxygen alkylated. As a result, the enthalpies of reaction were independent of cation, within experimental error. The sodium salt of dipivaloylmethane produced a significantly higher percentage of the carbon-methylated product, and thus had a higher heat of reaction. In THF, mixtures of the carbon-methylated and oxygen-methylated products were obtained, and the resulting enthalpies of reaction were easily interpretable in terms of the products (increasing carbon methylation resulted in more exothermic reactions). The most dramatic thermochemical result was the relative inactivity of LiDBM and LiDPM when treated with the highly reactive methylating agent methyl fluorosulfonate in PC, a solvent of high dielectric constant (ϵ 65) in which rapid, exothermic (26 kcal/mol) methylations of all the other enolates occurred. This observation may be attributable to kinetically stable ionic aggregates of the lithium enolates in PC. Our conductance results for LiDBM and LiDPM in Me₂SO indicate the formation of higher order aggregates, as do the ¹H NMR results of Raban¹ for lithium acetylacetonate in methanol. The results from all phases of this study are interpretable in terms of an ion-pairing model. The application of this model to the kinetics of alkylation of the ambident alkali β -ketoenolate in Me₂SO shows that the free anions are the primary reactive species in the second-order reactions which form both the carbon and oxygen alkylation products. A second mechanism dominates the oxygen methylation of the enolates in Me₂SO.

Introduction

The activation of carbonyl compounds by bases to produce enolate anions is one of the most important primary reactions in synthetic organic chemistry. Since alkali alkoxides or alkali amides are the most commonly used basic catalysts and the solvents employed are often of only moderate polarity, it is natural to suppose that enolate ions and alkali-enolate ion pairs are key intermediates in such processes. The dissociation of enolate ion pairs has been implicated by a number of authors²⁻⁶ in stereospecific or regioselective attack at carbonyl oxygen or the α carbon of the ambident enolate anion. Considerable evidence supports the notion that dissociated enolate anions are much more reactive than are the corresponding ion pairs.²⁻⁶ However, we know of no extensive physicoorganic chemical study which has brought to bear a variety of experimental methods to elucidate the nature of the ion pairs and to correlate their association rigorously with their nucleophilic reactivity in a well-characterized system.

Beyond the possible mechanistic value of such an investigation we have been concerned to examine the self-consistency of various methods which have been applied elsewhere to the study of ion pairs. With the exception of a few investigations⁷⁻¹⁰ the majority of reports concerning ion association have been limited to application of a single experimental technique to the system under study and thus afford little op-

portunity for independent checks on the reality of postulated species.

The present investigation has two aims which we have attempted to coordinate. The first is to elucidate the kinetics of alkylation of a well-characterized type of enolate anion in terms of ion pairing. The second is to use the enolate ion-pair system as a testing ground for the self-consistency of a variety of techniques which have been used previously to study associated electrolytes; such as conductance, kinetics, spectroscopy (UV, IR, NMR) and thermochemistry. Our results provide strong support for the generally accepted theory of alkylation^{5,11} of dissociated enolate anions. In addition, several unexpected results were observed.

Experimental Section

Sources and Purification. Most of the compounds used in the study are commercially available. Liquids were usually dried using an appropriate agent, and then doubly distilled. Solids were usually dried at 40 °C in a vacuum oven at \sim 1-mm pressure. All compounds were protected from light. Initially, purity was established by refractive index as measured by a Bausch and Lomb Abbe refractometer. A Du Pont 830 liquid chromatograph was also used to establish solvent purity. A Photovolt Model Aquatest II automatic titrator was used to measure water content by Karl Fischer titration. Acceptable water content was <50 ppm of water.

Dibenzo-18-crown-6 ether (Aldrich Technical Grade) was crys-

tallized three times from hot benzene and dried under vacuum at 60 °C for 12 h, mp 164 °C. Dibenzoylmethane (Aldrich) was purified by multiple crystallizations, first from petroleum ether and then twice from absolute methanol. Dicyclohexyl-18-crown-6 ether (Aldrich Technical Grade) was dissolved in hot hexane with decolorizing carbon and filtered while hot. This procedure was repeated until a colorless filtrate was obtained. The remaining crystals were filtered and dried at room temperature under vacuum for 24 h. Dimethyl sulfate (MCB) was stirred over sodium carbonate for 24 h, doubly distilled at 8-mm pressure using an 8-in. column packed with glass helices, and stored in the dark under argon. Dimethyl sulfoxide (Crown-Zellerbach or Aldrich) was stirred for 12 h under vacuum with 20 mL/L added of a 1.6 M *n*-butyllithium solution, additional *n*-butyllithium solution was then added, and the Me₂SO was doubly distilled at 1-mm pressure. The Me₂SO was then stored under argon in a taped solvent bottle fitted with an automatically zeroing buret. A positive pressure of argon was constantly maintained in the system. Dimethyl sulfoxide-*d*₆ (Norell, 99.5% D) was placed over activated Linde 4A sieves and stored under argon for a minimum of 48 h prior to use. Dipivaloylmethane (Aldrich) was purified by triple distillation via an 8-in. column packed with glass helices. Ethanol (U.S. Industrial Chemical Co., Absolute) was doubly distilled under argon from sodium. Hexamethylphosphoramide (Aldrich) was distilled under reduced pressure and stored in the dark under argon. Methyl iodide (Aldrich) was distilled through an 8-in. column packed with glass helices. The middle fraction was washed three times with an aqueous solution of sodium bisulfate, washed five times with water, and then stored over P₂O₅ for 24 h. The methyl iodide was then distilled from fresh P₂O₅ and stored in the freezer under argon. Methyl fluorosulfonate (Aldrich) was doubly distilled under argon through an 8-in. column packed with glass helices and stored in the freezer under argon. Methyl *p*-toluenesulfonate (MCB) was dried over anhydrous magnesium sulfate for 12 h, doubly distilled under reduced pressure, and stored in a freezer under argon. Potassium chloride (Fisher) was crystallized from distilled water, fused in a crucible, and stored in a desiccator under reduced pressure. Propylene carbonate (Aldrich) was refluxed for 12 h with calcium oxide, doubly distilled at 5-mm pressure, and stored under argon in a taped solvent storage bottle fitted with an automatic zeroing buret. Tetrahydrofuran (Aldrich) was refluxed for 24 h with lithium aluminum hydride to remove water, peroxides, and other impurities. It was then doubly distilled from sodium and stored in the dark under argon. *N,N,N',N'*-Tetramethylethylenediamine (Eastman) was refluxed for 12 h over potassium hydroxide and doubly distilled under argon. Tetramethylsilane (Merck Sharp & Dohm) was used without purification. Water (deionized) was distilled from a Corning Megapure still and double distilled. Prior to use for conductance measurements or use with the liquid chromatograph, this water was boiled while argon was bubbled through it.

Preparation of Alkali Enolates. Double distilled ethanol was distilled from sodium onto the desired alkali metal under argon. To the resulting ethoxide solution, an appropriate amount of the β -dicarbonyl compound was added (slight excess of ethoxide). After ~15 min the precipitated crystals were filtered and dried in a vacuum oven for 24 h at 40–60 °C.

Preparation of Tetrabutylammonium Dibenzoylmethide. A sample of sodium dibenzoylmethide was prepared as outlined above and placed in a 2:1 toluene–THF solution at 0 °C. An equimolar amount of tetrabutylammonium iodide was added, and the mixture stirred for 1 h. Precipitated crystals of sodium iodide were filtered. The solution was then cooled in a dry ice–acetone bath and filtered again. The THF was then stripped from the solution, and the resulting enolate–toluene solution was cooled. The precipitated enolate was filtered off and dried in a vacuum oven over at 40 °C for 12 h.

Because of the hygroscopic nature of these enolates and several of the solvents used, all work was accomplished under an argon atmosphere. When it was not convenient to purge an instrument with argon or nitrogen, sealed sample holders containing argon were used.

Infrared Spectroscopy. Infrared spectra of thin films of solutions, solid pellets, and solid mulls in the 2000–400-cm⁻¹ region were obtained from a Beckman IR-12 infrared spectrometer. Sealed, demountable KBr liquid cells were prepared and used in the solution study, and cesium iodide plates were used in the thin film study. Solid sample pellets were made from cesium iodide crystals. Solid mulls were made from both Nujol and fluorocarbons liquid agents.

Far-infrared spectra (100–550 cm⁻¹) for THF solutions of the enolates were determined with a Beckman IR-11. Polyethylene, sealed

Table I. Conductance of LiDBM in Me₂SO at 25 °C

[LiDBM] × 10 ⁴ , M	10 ⁶ /R, Ω ⁻¹	Λ, Ω ⁻¹ cm ³ M ⁻¹
1.357	0.2225	3.279
2.714	0.320	2.358
5.429	0.493	1.816
13.57	1.093	1.611
21.71	1.505	1.386
27.14	1.91	1.408
43.43	4.5	2.072
54.29	4.85	1.787

Table II. Conductance of KDBM in Me₂SO at 25 °C

[KDBM] × 10 ⁴ , M	10 ⁶ /R, Ω ⁻¹	Λ, Ω ⁻¹ cm ³ M ⁻¹
0.5954	0.915	30.73
0.7939	1.08	27.21
2.382	3.00	25.29
3.969	4.67	23.53
11.91	11.51	19.33
19.85	16.90	17.03
31.76	24.0	15.11
39.69	27.8	14.01
47.63	31.8	13.55
63.51	38.8	12.06
79.39	44.5	11.21

liquid cells were prepared and filled by first purging with argon, and then filling with solution (from 5 × 10⁻² to 1.5 × 10⁻¹ M) by means of a gas-tight syringe.

Magnetic Resonance Spectroscopy. Proton magnetic resonance spectra were determined with a Varian A60-D NMR spectrometer at its ambient temperature (35–45 °C). Standard 5-mm NMR tubes were used. All chemical shifts were referenced to the proton absorption of tetramethylsilane. Samples were prepared by dissolving the solid in the appropriate solvent in an argon-purged NMR tube. Sample concentrations ranged from 2 × 10⁻² M to 5 × 10⁻² M.

Carbon-13 magnetic resonance spectroscopy employed a JEOL FX-60 magnetic resonance spectrometer operating at 15.00 MHz. The instrument was used as a single-pulse Fourier-transform instrument with the proton absorption irradiated, and the instrument was locked on the main absorption frequency of deuterium in the solvent Me₂SO-*d*₆. Generally 4000–6000 pulses were obtained, with a Fourier transform followed by data storage after every 100 pulses. Spectral width was 5000 Hz, and 4096 data points were utilized with 8-μs pulse width and 3.0-s repetition. Spectra were obtained at ambient instrument temperature (25–30 °C), and chemical shifts were referenced to the carbon absorption of Me₄Si. Samples were prepared in 10-mm NMR tubes and over a concentration range of 2 × 10⁻² to 5 × 10⁻² M.

Ultraviolet Spectroscopy. Ultraviolet spectra were determined with a Cary Model 15 ultraviolet–visible spectrophotometer at ambient instrument temperature.

Results

In the interests of brevity we present primary data which we think are either necessary for the evaluation of our interpretations or which we believe may be of direct value to other experimentalists. More extensive tabulations are available.¹⁵

Conductance. Tables I and II contain the measured conductivity of Me₂SO solutions of LiDBM and KDBM, respectively. Column 2 presents the measured resistance. Column 3 lists the equivalent conductance, Λ. Table III presents the equivalent conductances at infinite dilution, Λ₀, the calculated dissociation constants, and the correlation coefficients of the plots of equivalent conductance vs. the square root of the product of degree of dissociation and concentration (Λ vs. (αc)^{1/2}).

Calculation of the Dissociation Constant. The Grunwald method¹⁶ for the calculation of the degree of dissociation of

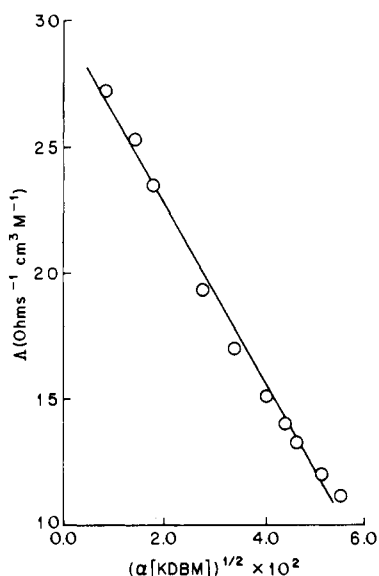


Figure 1. Equivalent conductance vs. the square root of the product of the degree of dissociation (α) and the molar concentration of KDBM.

Table III. Conductance of Univalent β -Ketoenolates in Me₂SO at 25 °C

Compd	$\Lambda_0, \Omega^{-1} \text{ cm}^2$	Corrn coeff	$K_d \times 10^4, \text{ M}^{-1}$
NaDBM	19.6 ± 2.0	0.918	1.61 ± 0.22
KDBM	29.7 ± 0.4	0.996	19.2 ± 0.7
CsDBM	29.8 ± 0.3	0.992	68.1 ± 3.5
Bu ₄ NDBM	30.8 ± 1.6	0.865	62 ± 24
NaDPM	10.0 ± 1.0	0.961	3.41 ± 0.76
KDPM	27.1 ± 1.2	0.970	7.47 ± 0.69
CsDPM	29.7 ± 0.3	0.996	36.9 ± 2.6

enolates was used rather than the Shedlovsky method¹⁷ which is more suitable at higher dilutions. The basic equations are

$$\alpha = \frac{\Lambda[1 + 2.303S(\alpha c)^{1/2}]}{\Lambda_0 \left[1 + 2.303(\alpha c)^{1/2} - \frac{S\Lambda}{\Lambda_0(\alpha c)^{1/2}} \right]} \quad (1)$$

$$S = \frac{1.825 \times 10^6}{(\epsilon T)^{3/2}} \quad (2)$$

$$S\Lambda = \frac{8.2 \times 10^5}{(\epsilon T)^{3/2}} \Lambda_0 + \frac{82.4}{\eta(\epsilon T)^{10}} \quad (3)$$

where α is the degree of dissociation, Λ_0 is the equivalent conductance at infinite dilution calculated from a Λ vs. $(\alpha c)^{1/2}$ plot, c is the molar concentration of the solute, T is the absolute temperature, ϵ is the dielectric constant of the solvent, and η is the viscosity of the solvent. An iterative program¹⁵ was utilized to achieve convergence when a plot of Λ vs. $(\alpha_i c_i)^{1/2}$ is linear. Figure 1 is such a graph of the equivalent conductance vs. the square root of the product of the degree of dissociation and the concentration of KDBM in Me₂SO. Convergence of the solution was determined by invariance of the calculated quantity Λ_0 . The quality of this type of analysis was evaluated through the linear correlation coefficient of the Λ vs. $(\alpha c)^{1/2}$ plot. The ion-pair dissociation constant (K_d) was derived from the degree of dissociation by the equation

$$K_d = \alpha^2 c / (1 - \alpha) \quad (4)$$

where c is the molar concentration of the solute.

Infrared. Table IV presents the important infrared absorption bands (in reciprocal centimeters) of the solid alkali dibenzoylmethides, tetrabutylammonium dibenzoylmethide,

Table IV. Important Infrared Absorption Bands (cm⁻¹) for Solid Dibenzoylmethides

HDBM	1600	1551	615		
LiDBM	1598	1546	1524	613	555
NaDBM	1605	1556	1515	610	527
KDBM	1603	1565	1507	610	515
CsDBM	1605	1561	1505	607	521
Bu ₄ NDBM	1606	1565	1510	610	505

Table V. Far-Infrared, Cation-Sensitive Absorption Band for Enolate-THF Solutions

	DBM		DPM	
	cm ⁻¹	kcal/mol	cm ⁻¹	kcal/mol
Li	433.71	1.24	426.73	1.22
Na	399.98	1.14	391.90	1.12
K	339.33	0.970	374.30	1.07
Cs	337.62	0.965	370.74	1.06
Bu ₄ N	351.00	1.00		

Table VI. Proton Magnetic Resonance Chemical Shift (δ) for the Methylene Protons of Alkali Enolates

	Me ₂ SO	Me ₂ SO + complexing agent	Me ₂ SO + excess cation	Acetone
	HDBM	7.32		
LiDBM	6.48	6.50	6.50	
NaDBM	6.37	6.36	6.33	6.43
KDBM	6.24	6.27		
CsDBM	6.14	6.12		6.32
Bu ₄ NDBM	6.29			
HDPM	5.86			
LiDPM	5.36	5.42		
NaDPM	5.28			
KDPM	5.22	5.25		
CsDPM	5.19	5.16		

and dibenzoylmethane. Listed in Table V is the cation-sensitive, far-infrared band of the THF solutions of the enolates (in reciprocal centimeters and kilocalories/mole).

Nuclear Magnetic Resonance. Table VI lists the position of the methylene proton absorption in proton magnetic resonance (¹H NMR) in parts per million (ppm) referenced to the proton absorption of Me₄Si. The conditions of the experiments are listed in the table. Excess cations were introduced as the salts of "inert" anions, such as perchlorates or hexafluorophosphates.

Table VII presents a natural-abundance, carbon-13 magnetic resonance data for the position of the carbonyl and methylene carbons absorption (in parts per million) referenced to the carbon absorption Me₄Si.

Ultraviolet. Table VIII shows the position (in nanometers) of the maximum ultraviolet absorption for the $\pi \rightarrow \pi^*$ transition (assigned by Cotton⁴⁵) for the alkali enolates and tetrabutylammonium enolates in various solvents in the presence and absence of complexing agents. The complexing agents used were TMEDA for the lithium ions, dicyclohexyl-18-crown-6 for sodium ions, and dibenzo-18-crown-6 for potassium and cesium ions.

Calorimetric Heats of Methylation. Table IX lists the calorimetric heat of methylation of the respective enolates. Methylfluorosulfonate was the alkylating agent, and the solvents were propylene carbonate (PC) and tetrahydrofuran (THF). Marked in parentheses is the percentage of carbon or oxygen alkylation measured by liquid chromatographic analysis and/or ¹H NMR analysis for these experimental conditions.

Kinetics of Alkylation. The temperature of the contents of an adiabatic cell, in which an alkylation reaction was in

Table VII. Carbon-13 Magnetic Resonance Chemical Shift (δ) of Carbonyl and Methylene Carbons of Dibenzoylmethides and Dipivaloylmethides

	Me ₂ SO		Me ₂ SO + complexing agents ^a		Me ₂ SO + cation	
	Carbonyl	Methylene	Carbonyl	Methylene	Carbonyl	Methylene
LiDBM	182.456	90.903	182.090	91.715		
NaDBM	182.090	90.477	182.089	90.638	182.253	90.639
KDBM	181.320	90.417	181.115	90.314	181.969	90.903
CsDBM	180.465	90.151				
Bu ₄ NDBM	181.765	90.476				
HDPM	201.276	90.964				
LiDPM	196.388	86.090	196.547			
NaDPM	195.410	84.953	195.410			
KDPM	194.597	84.791	194.436			
CsDPM	193.786	84.504				

^a Complexing agents used were TMEDA, dicyclohexyl-18-crown-6 polyether, and dibenzo-18-crown-6 polyether for Li⁺, Na⁺, and K⁺, respectively.

Table VIII. Ultraviolet Absorption $\pi_3 \rightarrow \pi^*$ (nm) for Alkali Dibenzoylmethides (DBM) and Dipivaloylmethides (DPM) in Various Solvents in the Absence and Presence (in Parentheses) of Complexing Agents^a

	HMPA	Me ₂ SO ₄	THF	CCl ₄	H ₂ O
LiDBM	355.4 (355.8)	361 (357.8)	358 (358)	312	352.5 (341)
NaDBM	351.0 (352.5)	360 (355)	354 (341)		
KDBM	352 (352)	365 (348)	357 (342)	338 (337.5)	343 (343)
CsDBM	352 (353)	364 (362.5)	340 (342)		
Bu ₄ NDBM	350	360	354	338	348
LiDPM		294 (281)	292 (288)	281,276 (291)	
NaDPM		295 (275.5)	273.5 (273.5)	283 (277)	
KDPM		297 (277.5)	275.5 (275.5)	276 (277.5)	278.5 (279.5)
CsDPM		297.5 (296, 285)	276.5 (277.5)	276.5 (277)	288.5 (288.5)

^a Complexing agents were tetramethylenediamine for Li⁺, dicyclohexyl-18-crown-6 for Na⁺, and dibenzo-18-crown-6 for K⁺ and Cs⁺.

Table IX. Calorimetric Heats of Methylation of β -Ketoenolates in Propylene Carbonate and Tetrahydrofuran with Methylfluorosulfonate^a

Compd	ΔH , kcal/mol (PC)	ΔH , kcal/mol (THF)
HDBM	No rxn	No rxn
LiDBM	No rxn	-29.6
NaDBM	-26.5 \pm 1.1 (98% -O)	-32.2 \pm 0.4 (67% -C)
KDBM	-25.8 \pm 10 (98% -O)	-36.5 \pm 0.4
CsDBM	-26.3 \pm 0.1	-34.9 \pm 1.6
HDPM	No rxn	No rxn
LiDPM	No rxn	-36.5 \pm 3.5
NaDPM	-34.7 \pm 0.6 (<90% -O)	-36.2 \pm 0.8
KDPM	-26.5 \pm 1.9 (>90% -O)	-40.3 \pm 0.9 (71% C)
CsDPM	-26.1 \pm 0.6 (>90% O)	-40.3 \pm 1.4 (83% C)

^a Concentrations: enolate \approx 0.02–0.05 M; MeSO₃F \approx 0.00309 M.

progress, was monitored as a function of time with a Tronac 1250 calorimeter and a strip chart recorder. The observed thermogram contains displacements due, not only to the reaction(s) of interest, but also to nonchemical terms. Corrections were made according to Eatough, Christensen, and Izatt,¹⁸ and the total procedure was checked against the published second-order rate constant for hydrolysis of ethyl acetate (0.134 s⁻¹ M⁻¹), our value being 0.137 s⁻¹ M⁻¹.

At any point p along a thermogram curve, the relationship between the measured heat ($Q_{\text{cor},p}$), ΔH° , and the extent of the reaction which has taken place is given by the equation

$$Q_{\text{cor},p} = \sum_{i=1}^m (\Delta H^\circ_i \cdot n_{i,p}) \quad (5)$$

$Q_{\text{cor},p}$ is the experimentally measured heat at point p due to all m reactions taking place in the calorimeter and corrected for all extraneous heat terms. ΔH°_i is the standard molar enthalpy of the i^{th} product formed at point p where $[A]_i$ and $[B]_i$ are the initial concentrations of the respective reagents. The integrated second-order, rate equation takes the form.

$$\ln \frac{1 - [(B]_i/[A]_i)(Q_{\text{cor},i}/Q_{\text{cor},\infty})}{1 - (Q_{\text{cor},i}/Q_{\text{cor},\infty})} = kt([A]_i - [B]_i) \quad (6)$$

A linear regression analysis was used to determine k . The slope of a plot of the left side of eq 6 vs. t is equal to $k([A]_i - [B]_i)$.

The rate expression for competing first- and second-order reactions used in treating the data for the alkylation reactions with methyl sulfate is written

$$dx/dt = k_1(A - x) + k_2(A - x)(B - x) \quad (7)$$

where x is the concentration of product formed.

Under proper conditions,¹⁹ k_1 and k_2 may be obtained simply by rearranging the above equation to

$$(dx/dt)/(A - x) = k_1 + k_2[B - x] \quad (8)$$

which may be solved by linear regression analysis of $(dx/dt)/(A - x)$ as a function of $(B - x)$. The resultant slope is equal to k_2 and the intercept is equal to k_1 .

The differential rate, dx/dt , was obtained by plotting x as a function of time. A mirror was placed at a point p on the curve, and its plane adjusted until the curve and its reflection joined with no point of inflection. A line segment was then drawn along the edge of the mirror, which was normal to the curve. The procedure was repeated, and a line segment was drawn normal to the first line segment. This second line segment is parallel to the tangent to curve at point p , and the slope of this line segment is dx/dt at point p . This procedure was repeated at selected intervals of the reaction.

Table X lists typical data for the reaction of methyl iodide with potassium dibenzoylmethide in Me₂SO at 25 °C. Also contained in this table is the concentration of the free anion calculated by the equation

$$K_d = ([K^+][DMB^-])/[KDBM] \quad (9)$$

where $[K^+]$, $[DBM^-]$, and $[KDBM]$ are the molar concen-

Table X. Kinetics of Methylation of KDBM with Methyl Iodide in Me₂SO

[KDBM] × 10 ³ , M	[CH ₃ I] × 10 ² , M	k ₂ , s ⁻¹ M ⁻¹	[Free anion] × 10 ³ , M	k ₂ [KDBM] × 10 ³ , s ⁻¹
0.2076	4.24	0.798	0.1890	0.1657
0.5295	6.006	0.570	0.4320	0.3018
1.341	6.237	0.360	0.9093	0.4828
1.631	5.036	0.347	1.052	0.5660
2.573	11.71	0.304	1.460	0.7745
7.543	8.792	0.192	2.962	1.448
10.95	13.64	0.149	3.721	1.630
14.52	13.73	0.136	4.402	1.975
19.52	15.98	0.137	5.231	2.674

Table XI. Kinetics of Methylation of KDBM with Methyl Iodide in Me₂SO with Added Agents

[KDBM] × 10 ³ , M	[DBM ⁻] × 10 ³ , M	k ₂ , s ⁻¹ M ⁻¹	[KClO ₄] × 10 ² , M	k ₂ [KDBM] × 10 ³ , s ⁻¹
2.232	0.5971	0.158	0.4646	0.3515
2.354	0.2245	0.107	1.793	0.2528
2.468	0.131	0.0814	3.404	0.2009
2.508	0.0610	0.0639	7.677	0.1628
			[Dibenzo-18-crown-6] × 10 ³ , M	
5.918	2.560	0.269	16.67	1.609
9.870	3.494	0.186	7.149	1.836
12.35	3.999	0.159	6.329	1.964
			Mol % H ₂ O	k ₂ [KDBM]/[anion], s ⁻¹ /M ⁻¹
4.431	2.109	0.200	0	0.420
4.014	1.976	0.206	0	0.418
4.857	2.239	0.193	0.959	0.419
3.942	1.917	0.200	1.92	0.403
3.404	1.769	0.204	3.70	0.393
2.682	1.503	0.220	3.84	0.392
5.372	2.390	0.130	10.95	0.293

Table XII. Kinetics of Methylation of KDBM with Dimethyl Sulfate in Me₂SO

[KDBM] × 10 ³ , M	[(CH ₃ O) ₂ SO ₂] × 10 ² , M	k ₂ , s ⁻¹ M ⁻¹	[DBM ⁻] × 10 ³ , M	k ₂ [KDBM] × 10 ³ , s ⁻¹
3.378	7.915	0.395	1.760	1.333
5.015	7.040	0.262	2.286	1.312
7.181	8.137	0.202	2.872	1.454
8.639	6.858	0.156	3.221	1.349
8.831	5.127	0.168	3.265	1.481

Table XIII. Kinetics of Methylation of KDBM with Dimethyl Sulfate in Me₂SO by Competing Mechanisms

[KDBM] × 10 ³ , M	k ₂ , s ⁻¹ M ⁻¹	k ₁ , s ⁻¹	k ₂ [KDBM] × 10 ⁴ , s ⁻¹
3.378	0.168	3.33 × 10 ⁻⁴	5.675
5.015	0.107	3.22 × 10 ⁻⁴	5.366
7.181	0.0854	3.76 × 10 ⁻⁴	6.132
8.639	0.0846	4.28 × 10 ⁻⁴	7.308
8.831	0.0673	5.01 × 10 ⁻⁴	5.943

trations of free potassium ion, free DBM ion, and the ion-paired species, respectively. K_d is the conductometric dissociation constant obtained from Table III. In addition, this table lists the product of the observed second-order rate constant and the initial salt concentration.

Table XI presents typical data for the reaction of methyl iodide with KDBM in Me₂SO at 25 °C in which the effect on the rate of reaction by added reagents was investigated. These reagents were potassium perchlorate, dibenzo-18-crown-6 ether, and water.

Table XII presents results for the reaction of dimethyl sulfate with KDBM, respectively, in Me₂SO at 25 °C in terms of a single second-order reaction.

Table XIII presents results from recalculation of the kinetics described in Table XII. The procedure, of Young and An-

draws,¹⁹ allows for the second-order reaction of dimethyl sulfate with enolate as well as first-order reaction of dimethyl sulfate with the solvent Me₂SO. The first-order reaction between (CH₃O)₂SO₂ and Me₂SO results in the formation of the extremely reactive alkylating agent dimethylmethoxysulfonium methyl sulfate. This sulfonium salt reacts with the enolate "instantly" to form the methyl vinyl ether of the β diketone.

Our most extensive kinetic studies were performed with KDBM and are tabulated elsewhere in detail.¹⁵ Equivalent runs were also made with NaDBM but the results are not tabulated here to conserve space.

Discussion

This article is concerned primarily with the relationship between the structures of alkali β-ketoenolates in nonhydroxylic solvents and their reactivity as ambident nucleophiles. A logical order of priorities would present structural evidence first and then consider the implications of such evidence to energetics in terms of thermochemistry and rate data. However, we will consider our conductance data immediately since they provide the classical criteria for distinguishing between nonconducting and conducting species and are therefore necessary for interpreting all the rest of our results.

Conductance. The fundamental basis for discussion of ion pairing was laid by electrochemists and has been the subject

Table XIV. Calculated Bjerrum Distances for Alkali and Tetrabutylammonium Enolates in Me_2SO

Salt	K_d, M^{-1}	$a, \text{\AA}$
NaDBM	1.614×10^{-4}	0.776
KDBM	1.914×10^{-3}	0.975
Bu_4NDBM	6.516×10^{-3}	1.12
CsDBM	6.18×10^{-3}	1.13
NaDPM	3.14×10^{-4}	0.826
KDPM	7.47×10^{-4}	0.887
CsDPM	3.69×10^{-3}	1.05

of several recent reviews.⁷⁻⁹ The relevance of ion pairing to reaction mechanisms has been recognized for some time²⁴⁻²⁶ but did not receive general attention until the researches of Winstein²⁷ and Szwarc.^{8,9} However, despite the synthetic importance of enolate anions and the well-authenticated structures of β -ketoenolate anions, relatively few published accounts of their electrochemical behavior are to be found.^{6,13,28-30} Indeed, none are referenced in any of the primary review sources on ion-pairing listed above. More popular subjects of ion-pairing studies have been inorganic salts of alkali and alkylammonium ion and resonance-stabilized carbanions and related anion radicals.

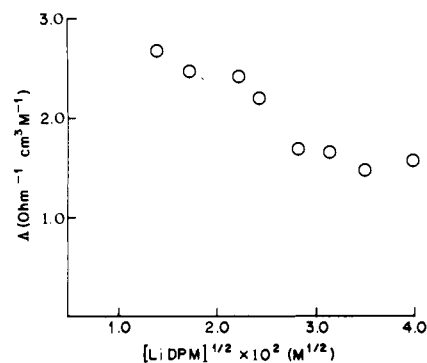
Results presented in Tables I-III were obtained with a 1% bridge and are not to be considered of high precision. We believe, however, that they are quite adequate for most of the purposes to which they will be applied below.³¹

Comparison of the data for LiDBM (Table I) with those for KDBM shows the very slight conductance of the lithium compound, even though Li^+ interacts strongly with Me_2SO . Furthermore, what conductance there is varies only slightly with concentration changes suggesting that the nonconducting species are fairly large aggregates instead of just ion pairs. This interpretation follows those of Friedman³² and Yeager³³ for similar results for lithium trifluoroacetate in propylene carbonate.

Although our data for the lithium compounds are of marginal precision, one notes from Figure 2 a small, but apparently real increase in conductance at higher concentrations. This may be attributed to the formation of triple ions, such as $\text{Li}_2\text{DBM}^+\text{Li}(\text{DBM})_2^-$, corresponding to analogous species proposed by Raban and Noe¹ on the basis of NMR experiments. Triple ions are considered to have somewhat greater mobilities than the corresponding heavily solvated single ions.

The dissociation constants for the alkali dibenzoylmethides show a change by a factor of 42 on going from Na^+ to Cs^+ . The dissociation constants show that alkali dipivaloylmethides are less sensitive than dibenzoylmethides to variation of cation in Me_2SO . The change in calculated dissociation constant on going from Na^+ to Cs^+ for the dipivaloylmethides is a factor of 10. However, one could be skeptical of the NaDPM result. It seems somewhat obvious that the limiting equivalent conductance (Λ_0) is too low; a value of ~ 20 could be expected.^{13,28} This discrepancy may be due to experimental problems or may be due to the formation of higher aggregates, as is suspected for the lithium compounds.

The value of the dissociation constant for Bu_4NDBM is intermediate between that of KDBM and CsDBM. Tetrabutylammonium salts are often included in conductance studies of alkali metal salts in dipolar aprotic solvents.^{28,34} Recent investigators of the conductance and ion solvent interactions of quaternary ammonium salts in Me_2SO have concluded that the tetrabutylammonium salts studied are completely dissociated^{35,36} and that the Bu_4N^+ ion does not interact strongly with the solvent.³⁶ In contrast, we find that ion pairing of Bu_4NDBM is comparable with that of the K^+ and Cs^+ cases.

**Figure 2.** Plot of the equivalent conductance vs. the square root of the molar concentration of LiDBM.

However, this is somewhat analogous to a study by Szwarc et al.³⁴ which reported dissociation constants of alkali and tetrabutylammonium tetraphenylborides in THF. The dissociation constant of Bu_4NBPh_4 was found to be intermediate between that of the Na^+ and K^+ salts. However, the results for Swarc's system (THF solvent) do not correlate entirely with ours since he reported the Na^+ salt to be most dissociated and the cesium salt the most associated.

Interionic Distance Parameter, a . The application of the Bjerrum theory has been successful in interpreting the properties of many electrolyte solutions.^{22,37} One feature which has been discussed extensively is the physical significance of the factor a in the Bjerrum equation. This was taken by Bjerrum³⁸ to be the distance of approach of two ions which are paired, and it was considered to be a variable quantity.

Despite some controversy regarding the meaning of the a factor,^{22,39-41} there is agreement³⁷ that the calculation of a , using a Bjerrum-type equation, will give some information as to the structure of the electrolyte solution. The results presented in Table XIV were obtained from the Fuoss modification of Bjerrum's equation.⁴⁰

These calculated distances are smaller than the crystallographic radii of the respective cations themselves. Fernandez-Prini and Prue⁴² obtained similar results for alkali metal salts in sulfolane and ascribed the small interionic distances to dielectric saturation of the solvent in the region of the ions. From their method of correcting for this effect, one would expect the corrected values of a to vary from 2.2 \AA for NaDBM to 4.4 \AA for Bu_4NDBM and CsDBM. The size of these calculated values of a implies that the structure of these ion pairs is a contact ion pair. Other workers^{23,35,42,43} have treated analogous results and have reached similar conclusions.

Spectral Studies. As prototype chelate compounds, the metal β -diketonates have been subjected to extensive structural study. Although there is analogy to aromaticity in some of their behavior, the original proposal of benzenoid resonance by Calvin and Wilson⁴⁴ has been considerably modified by Cotton.^{45,46} Despite a relative abundance of information about transition metal acetylacetonates from x-ray crystallography, it is only in the last 2 years that a successful study of an alkali compound— Li acac ⁴⁷—has been accomplished.⁴⁸ We therefore have very little precedent for considering the structures of undissociated alkali β -ketoenolates in solution. Our results suggest that they are primarily ion pairs, or aggregates thereof, rather than compounds analogous to the transition metal chelates, which employ d orbitals, rather than pure electrostatic interactions.

Infrared Spectroscopy. The β -ketoenolates have been of interest to inorganic chemists for many years, since they complex readily with transition metals. As a result, the infrared spectra of these compounds have been investigated extensively and band assignments made.

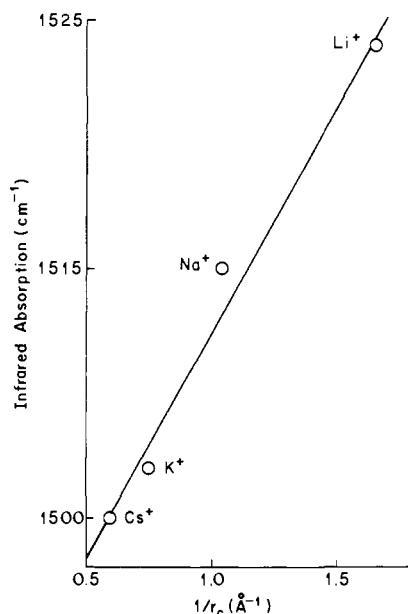


Figure 3. Infrared absorption frequency of the solid alkali dibenzoylmethides vs. the inverse of alkali cation radius (Pauling).

Table IV contains the bands of interest in the solid dibenzoylmethides in cesium iodide pellets, Nujol mulls, and fluorocarbon mulls. These bands are all sensitive to variation of cation, but none varies directly with the ionization potential of the parent metal of the respective cations.⁴⁹ The third band listed in Table IV, absent in the starting material dibenzoylmethane, is assigned to the carbonyl group.⁵⁰⁻⁵² Figure 3 is a graph of the frequency of this absorption vs. reciprocal of cation radius for the solid alkali dibenzoylmethides. It has been suggested⁴⁹ that, as the metal-oxygen bond strengthens, the carbonyl bond weakens, and thus its stretching frequency is lowered. Since the metal-oxygen attraction is electrostatic, it is not surprising that there is a correlation with interionic distance. Recently, bands of this type have been reported for alkali carbonylates¹⁰ and for lithium derivatives of acetonitrile.⁵³

Another infrared region of interest is the 600-200-cm⁻¹ region. Dismukes et al.,⁵⁴ in studying metal acetylacetonates, reported that there is no simple relationship between the infrared spectra of metal acetylacetonates below 700 cm⁻¹ and oxidation state, chemical character of the metal, or structure of the complex. They concluded that no absorption band can be assigned to a pure metal-to-oxygen vibration. Hancock and Thorton⁵⁵ reported four absorption bands below 650 cm⁻¹ and stated that all four bands vary in the same manner with variation of metal. They concluded that any of these bands could be assigned to the metal-to-ligand vibration. However, the bands listed in the last two columns of Table IV cast doubts on both of these interpretations. Obviously, these two bands do not behave in the same manner; i.e., one is present in the starting material. Further work would be necessary to show that it is indeed a metal-oxygen vibration.

Listed in Table V is a cation sensitive, far-infrared absorption band for THF solutions of the enolates. We have assigned this band to a cation-anion vibration⁵⁶ since it is also anion dependent and is not found in the far-infrared spectra of the respective starting materials. These frequencies do not correlate with the reduced mass of either the entire formula compound or of the six-membered chelate ring. However, when these frequencies were plotted against the reciprocal of alkali cation radius (Pauling), a good linear correlation was obtained (DPM, $r = 0.994$; DBM, $r = 0.962$). This is shown in Figure 4. Some precedent may be cited in the assignment of far-in-

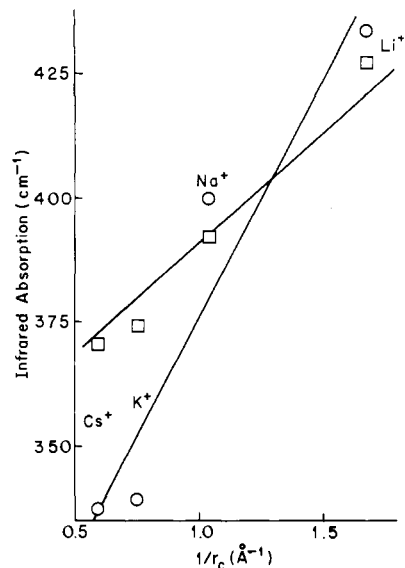


Figure 4. Plot of the far-infrared absorption (cm⁻¹) of the alkali β -ketonolates in THF vs. the inverse of Pauling alkali cation radii: O, DBM; \square , DPM.

frared bands to ion pairs for alkali cobalt carbonylates⁵⁷ and for tetraalkylammonium halides.^{58,59}

The slope of the line for the dibenzoylmethides is much greater than the slope of the line for the dipivaloylmethides. This may imply greater electronic delocalization in the dibenzoylmethide ion than the dipivaloylmethide ion.

The band reported here contrasts with those reported by others for ion-solvent vibrations.⁶⁰⁻⁶² Our reported band is sensitive to variation of both cation and anion. In addition, the range of frequencies is much smaller.

The position of the band for the tetrabutylammonium ion is surprising in view of its size in comparison to Na⁺ and K⁺. Far-infrared bands for cation-anion vibrations of tetrabutylammonium salts have been reported by other workers^{58,63} In addition, Popov⁶⁴ reported that cation-solvent bands for Na⁺ and NH₄⁺ in Me₂SO are similar. Therefore, if we assume that cation-anion bands follow the same pattern, and that alkylation of the ammonium ion causes a shift to lower frequencies by increasing the mass of the cation and the cation-anion distance, the position of the reported band of Bu₄N⁺ with respect to Na⁺ is reasonable. In addition, the effective radii of loosely solvated alkali cations are undoubtedly greater than their Pauling radii. Because of the greater size of the Bu₄N⁺ ion, it is plausible that it can take advantage of the bidentate nature of the anion, in a manner not available to the smaller alkali cations. It is easy to envision the orientation of a Bu₄N⁺ ion above the plane of the enolate, attracted simultaneously to the partial negative charges on both oxygens. In contrast, one would expect the alkali ion to lie closer to the plane of the enolate with tight external solvation, either flickering between the oxygen atoms, or attracted mainly to one oxygen atom.

Nuclear Magnetic Resonance. Both ¹H and ¹³C NMR spectra of the alkali enolates have been determined in Me₂SO-*d*₆. The results are listed in Tables VI and VII.

With regard to the proton magnetic resonance spectroscopy, one notices immediately that there is an upfield shift which again correlates with the reciprocal of the alkali cation radius (Pauling), as is seen in Figures 5 and 6. The addition of complexing agents causes a downfield shift in the chemical shift of the methylene proton for lithium and potassium salts, but an upfield shift for sodium and cesium salts of dibenzoylmethane. Added excess sodium ion causes an upfield shift in the position of the methylene proton.

The correlation of the chemical shift with the inverse of

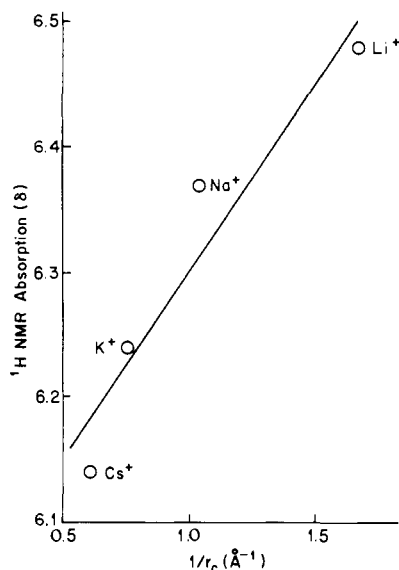


Figure 5. ^1H NMR chemical shift (δ) of the alkali dibenzoylmethides in $\text{Me}_2\text{SO}-d_6$ vs. the inverse of alkali cation Pauling radii.

cation radius may be taken as further evidence for the existence of contact ion pairs.

^{13}C NMR Spectra. Recently House et al.⁶⁵ have reported that natural abundance ^{13}C NMR spectra of metal enolates in a variety of solvents are sensitive to solvent changes, variation of cation, and the use of complexing agents. Furthermore, by the use of coupling constants, they concluded that the α -carbon atom of the enolates is in the plane established by the sp^2 carbons. In a report⁶⁶ of the ^{13}C NMR spectra of sodium salts of diethylalkyl-substituted malonates in $\text{Me}_2\text{SO}-d_6$, it was concluded that the ion pairs undergo rapid equilibrium on the NMR time scale.

The ^{13}C NMR spectra (Table VII) of the β -ketoenolates in $\text{Me}_2\text{SO}-d_6$ exhibit upfield shifts with increasing cation radius for both the carbonyl and methylene carbons. One of the factors responsible for an upfield shift of the ^{13}C NMR signal for an sp^2 carbon atom is an increase in π -electron density at the carbon.^{65,66} This implies that, as the cation radius enlarges, the electron density at the carbonyl and methylene carbons increases owing to increasing delocalization of charge throughout the ring. In addition, the direction of the shift implies that the cation-anion interaction is directed through the oxygens. Furthermore, since there is only one carbonyl absorption, this cation-anion interaction is through both oxygens simultaneously or through an equilibrium between two species. Since the infrared spectra of the solid enolate shows both a normal carbonyl absorption and a cation-sensitive absorption, also assigned as a carbonyl stretching frequency, one may favor the rapid equilibrium explanation. The ^{13}C chemical shifts do not correlate with the inverse of cation radius.

With only one exception, the addition of complexing agents had negligible effect on the chemical shift of the carbonyl carbon. Likewise, complexing agents had negligible effects on the ^1H NMR chemical shifts of the methylene proton. The exception mentioned above was the 0.812-ppm downfield shift of the methylene carbon of LiDBM in $\text{Me}_2\text{SO}-d_6$ upon addition of the complexing agent tetramethylethylenediamine (TMEDA). Since there is no effect on the chemical shift of the carbonyl carbon, one could propose that this change in chemical shift, and its implied change in chemical environment, may be due to a breaking up of large aggregates formed in lithium enolate systems.^{2,32,33} Possible explanations for this insensitivity of chemical shift to the addition of crown ethers

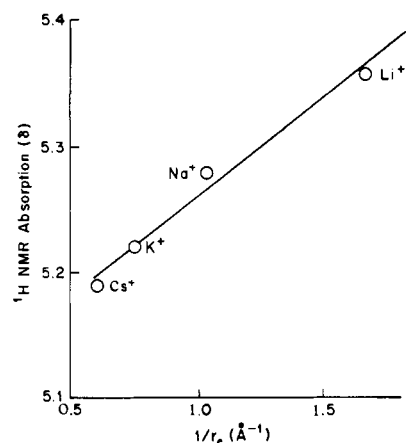


Figure 6. ^1H NMR chemical shift (δ) of the alkali dipivaloylmethides in $\text{Me}_2\text{SO}-d_6$ vs. the inverse of alkali cation Pauling radii.

are similar to those which will be discussed below under Kinetics.

Ultraviolet Spectroscopy. Many previous studies have been devoted to the measurement and interpretation of the electronic spectra of enolates,^{67,68} phenolates,⁶⁹ and β -ketoenolate metal chelates.^{45,67,70} Although the majority of the latter have been limited to transition-metal chelates, Garst⁶⁹ and Zaugg and Schaefer⁶⁷ have included some alkali chelates in their studies. Lacking direct precedents, we expected, on the basis of several spectral studies of ion pairing,^{67,71-73} that ultraviolet spectra might be a sensitive and informative method for examining ion pairing in the alkali β -ketoenolates. Our results listed in Table VIII show that we were mistaken.

Although substantial solvent shifts were found, there are remarkably small cation effects compared with those in related systems.⁶⁹ The solvent shifts do not correlate either with Kosower Z values⁷⁴ or with Gutmann donicity numbers⁷⁵—the most obvious solvent polarity parameters. The effects of added complexing agents (TMEDA and crown ethers) is mostly without significant effect on the spectra although some modest hypsochromic and bathochromic shifts are seen relative to λ_{max} for the salt of the uncomplexed cation. The results are uninformative compared to those of other workers^{76,77} which gave clear evidence, not only of ion pairing, but also allowed some discrimination between contact ion pairs and solvent separated ones. We record two peaks (at 285 and 296 nm) for CsDPM in Me_2SO with dibenzo-18-crown-6 which may represent two species of ion pairs. However, in view of the unsystematic behavior of our other UV results, we do not wish to press the point.

Highly dissociated alkali salts, such as perchlorates, hexafluorophosphates, and tetraphenylborates, were added with the expectation of increased ion pairing, as evidenced by hypsochromic shifts of λ_{max} . No effect was seen for the dipivaloylmethides, but blue shifts were noted for NaDBM and KDBM in Me_2SO and for NaDBM in THF.

Heats of Methylation. Table IX lists the calorimetrically determined heats of alkylation of the alkali enolates in propylene carbonate (PC) and tetrahydrofuran (THF). Aliquots of neat methylfluorosulfonate ("Magic Methyl") were added via syringe to solutions of excess enolate in the appropriate solvent. The aim was to investigate the possibility of determining differences in the heat of methylation of these enolates which would be relatable to ion pairing.

In propylene carbonate, the heats of methylation of NaDBM, KDBM, CsDBM, KDPM, and CsDPM, are identical, within experimental error. Liquid chromatographic analysis showed nearly complete oxygen methylation for these compounds under these conditions. Analysis showed that

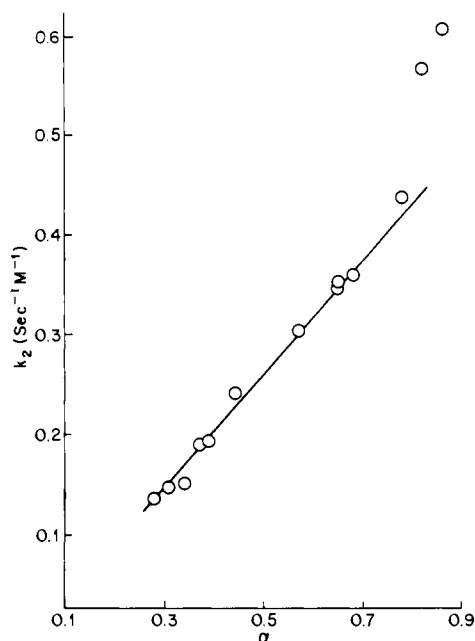


Figure 7. Calculated second-order rate constant (k_2) for the methylation of KDBM with methyl iodide in Me_2SO vs. the degree of dissociation (α) of the KDBM solutions.

methylation was not taking place entirely on the active oxygen site, but was also occurring on the carbon to a measureable extent.

Perhaps the most interesting result of these experiments is the relative inertness of the lithium compounds within the time scale of the experiments. Although the other alkali chelates reacted at clearly different rates (see below), their total heats of reactions were evolved within 2 min, whereas the lithium compounds showed no change within 0.5 h. This is somewhat surprising since the conditions of the experiment should favor reactivity: a solvent of high dielectric constant ϵ 65 and an extremely reactive alkylating agent. Wu and Friedman³² reported the enthalpies of solvation of alkali trifluoroacetates in propylene carbonate, a somewhat analogous system, and found the heat of solution of the lithium compound to be quite different from the heats of solution of the other alkali trifluoroacetates. In addition, the conductance^{32,33} of their system implied not only the existence of ion pairs but also a large proportion of higher aggregates which presumably are rather inactive.

The anomalous behavior of lithium compounds has occasionally led to the suggestion that these compounds actually form covalent bonds from lithium to the anion. Recently, the nature of the bond between lithium- and oxygen-containing ligands has received a considerable amount of theoretical treatment.⁷⁸ Such bonds are now believed to be ionic in nature. In a somewhat related system, Streitweiser⁷⁹ has shown that the lithium-carbon bond of methyl lithium is ionic.

Calorimetric heats of methylation were also obtained for the enolates in THF. The measured heat of methylation varied with both the nature of the cation and anion. However, the variation of the ratio of oxygen to carbon alkylation was not constant, and the heats of methylation are easily interpretable in terms of C/O alkylation product ratios.

In contrast to the experiments described above in propylene carbonate, the lithium enolates react slowly with methyl fluorosulfonate in THF solutions at 25 °C. Since THF strongly^{34,39,78} solvates lithium cations, the previously described large aggregates formed in PC^{32,33} would not be expected to form in THF.

The conclusions from the thermodynamic study of the heats

of methylation of the enolates in PC and THF may be summarized as follows. (1) When products are identical, no cation effect on the heats of methylation can be determined by this method; this implies that heats of ion pairing are too small to be detected in the presence of the very large exothermic heats of alkylation. (2) The different rates at which the heats of alkylation are liberated suggests that the rates of alkylation may be followed calorimetrically. Comparison with attempts to follow the rates by proton NMR and by UV spectroscopy confirmed the superiority of the calorimetric technique. (3) The lithium enolates do not react in PC, and this result may be due to the formation of stable aggregates. (4) Although lithium enolates are unreactive in propylene carbonate, their reaction with methyl fluorosulfonate in THF implies^{34,39} that specific solvent-ion interactions are important.

Kinetics of Methylation. The synthetic importance of enolate alkylation has motivated many studies of product distribution (oxygen vs. carbon alkylation) and some rate studies. The results and theoretical interpretations have been discussed in a number of reviews.^{2,3,5,6} A recent and comprehensive discussion by LeNoble⁵ relates the oxygen to carbon alkylation ratio to the degree to which the anion is encumbered from ion pairing or hydrogen bonding, so that oxygen alkylation takes precedence in dipolar aprotic solvents and carbon alkylation in protic ones. Our results presented below are basically consistent with this generalization which pictures the anion as the primary reactive species. Kornblum,⁴ Zaugg,⁸¹ Ugelstad,⁸² Zook,⁸³ House,³ and LeNoble⁵ and their colleagues have contributed considerably to our understanding of solvent and cation effects in such systems.

We have shown in preceding sections of this discussion how evidence of ion pairing from conductance correlates with that from several types of spectroscopy. We now wish to apply it to the elucidation of rate and product studies following precedents from the work of Reutov,⁶ Brandstrom,³⁰ and Smith.⁸⁴ The kinetics of methylation of potassium dibenzoylmethide with methyl iodide in Me_2SO at 25 °C are presented in Table X. One obtains 100% carbon alkylation of the β -ketoenolate under these conditions, as shown by ¹H NMR analysis. Figure 7 is a graph of the observed rate constant k_2 for the carbon alkylation of KDBM with the methyl iodide in Me_2SO as a function of the degree of dissociation (α) for the initial concentration of KDBM in Me_2SO from Table X. Following Acree's suggestion²⁵ that the observed rate of disappearance of enolate includes components from the reaction of methyl iodide with the "free" anion, An^- , and with the ion pair, M^+An^- , then we may write

$$\text{rate} = k_2[\text{MeI}][\text{salt}] \quad (10)$$

$$\text{rate} = k_i[\text{MeI}][\text{An}^-] + k_{ip}[\text{MeI}][\text{M}^+\text{An}^-] \quad (11)$$

where k_2 is the observed second-order rate constant, k_i and k_{ip} are the corresponding constants for reaction of the anions and the ion pairs, respectively, and [salt] is the stoichiometric concentration of the metal enolate.

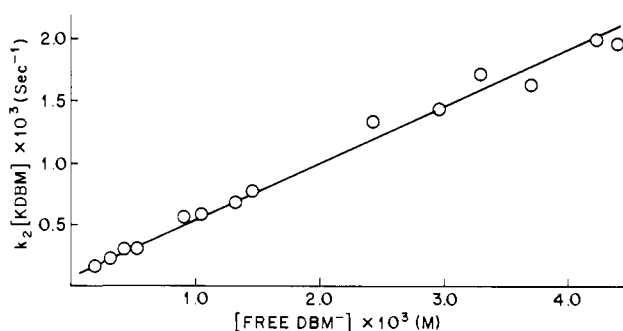
Combining eq 10 and 11 gives

$$k_2[\text{salt}] = k_i[\text{An}^-] + k_{ip}[\text{M}^+\text{An}^-] \quad (12)$$

If $k_i \gg k_{ip}$ a plot of $k_2[\text{salt}]$ vs. $[\text{An}^-]$ should be linear across a range of concentration where the concentration of anions and ion pairs are roughly comparable. Figure 8 is such a plot for KDBM. The nonzero intercept of Figure 8 demonstrates that the ion-pair term on the right in equation 14 is not negligible as $[\text{An}^-]$ becomes small. Its good linearity implies that k_{ip} is indeed so small that the second term is insignificant compared with the first across most of the range. Statistical information about the linear treatment of Figure 8 and corresponding plots for NaDBM and Bu_4NDBM are given in Table XV. Estimates of k_{ip} are also given derived from points on the line close to the

Table XV. Results of a Plot of k_2 [MDBM] vs. [Free Anion] for the Reaction of Methyl Iodide with Sodium, Potassium, and Tetrabutylammonium Dibenzoylmethide in Me_2SO

Salt	Corr coeff	Slope = k_i , $\text{s}^{-1} \text{M}^{-1}$	Intercept, s^{-1}	k_{ip} (est), $\text{s}^{-1} \text{M}^{-1}$
NaDBM	0.991	0.264	2.02×10^{-5}	0.103×10^{-4}
KDBM	0.990	0.464	7.93×10^{-5}	8.05×10^{-4}
Bu_4NDBM	0.986	0.110	11.1×10^{-5}	1.04×10^{-4}

**Figure 8.** Product of the calculated second-order rate constant (k_2) for the methylation of KDBM with methyl iodide in Me_2SO vs. molar concentration of the unpaired dibenzoylmethide anions.

intercept. As seen from eq 12, the slopes of the plots correspond to k_i , the rate constants for the free anions.

If the anions were indeed "free" we should have the same slope for each plot. The different slopes in Table XV suggest that there is some additional interaction between the cations and the DBM^- anions which is kinetically significant and which complicates the simple picture of only two reactive species—"free" and paired enolate anions. Unfortunately, our conductance data are of such low precision that the differences in slope might be the result of errors in our ion pair dissociation constants K_d which were used to calculate the concentrations of conducting ions. A referee has suggested an alternative explanation for this discrepancy. A shortcoming of our calculation of K_d (eq 4) is the assumption of unit activity coefficient. We recognize this approximation but would rather defer further investigation of this aspect of the problem until more accurate conductivity data become available.³¹ However, it remains a definite possibility that the apparent cation dependence of k_i in Table XV is the result of the involvement of a different reactive species such as a solvent-separated ion pair. If so, the order of reactivity of these species is different from those of the ion-paired species which are detected by the non-zero intercepts and which are listed under k_{ip} . The latter are three or four orders of magnitude less reactive than are the free anions. Thus, the NaDBM ion pair is much less reactive than is the Bu_4NDBM ion pair which in turn is about eightfold less reactive than the KDBM ion pair. This is the same order for the cation-anion vibrations in THF as solvent.

A further search for the presence of other reactive ion pairs was pursued by investigating the mass law effect of a common ion salt on the rate. Figure 9 shows the comparison of a plot of k_2 vs. α , the degree of dissociation in the presence and absence of added potassium perchlorate. The conductance data of Sears et al.⁴⁰ indicates that this salt is completely dissociated in Me_2SO at these concentrations. Equation 12 may be expressed as

$$k_2 = \alpha k_i + (1 - \alpha)k_{ip} \quad (13)$$

Since the latter term is relatively small at most values of α , a plot of k_2 vs. α should be linear with slope k_i . Figure 9 shows that the slope is essentially the same in the presence and absence of KClO_4 and thus that the anionic reaction rate, k_i , is not affected detectably by added K^+ .

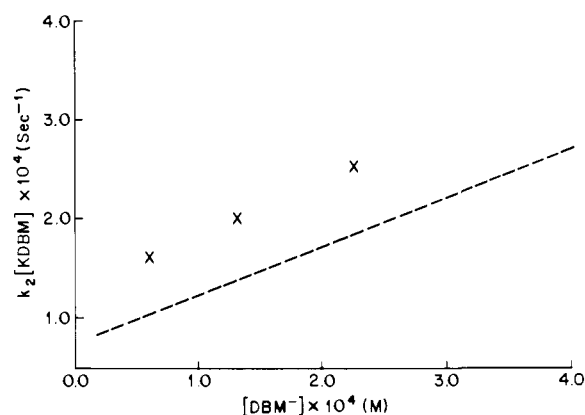
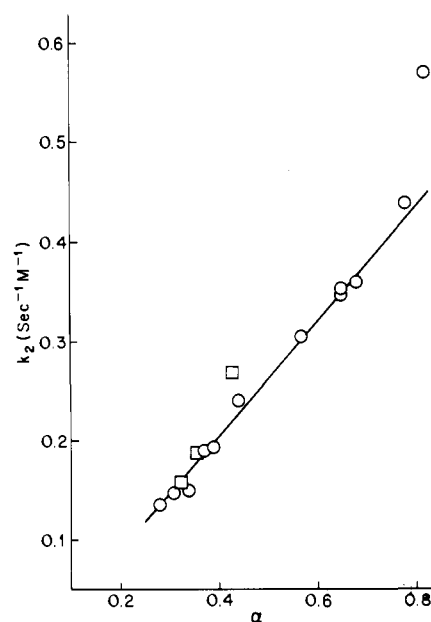
**Figure 9.** Product of the calculated second-order rate constant (for the methylation of KDBM with methyl iodide in Me_2SO with added potassium perchlorate and potassium hexafluorophosphates) and the molar concentration KDBM vs. the molar concentration of the unpaired dibenzoylmethide.**Figure 10.** Calculated second-order rate constant (k_2) for the methylation of KDBM with methyl iodide in Me_2SO with added dibenzo-18-crown-6 vs. the degree of dissociation (α) of the KDBM solutions.

Table XI and Figure 10 demonstrate the negligible effect of adding a crown ether complexing agent to the reaction of methyl iodide with KDBM in Me_2SO . In contrast to the reports of other authors,^{7,85,86} there was no effect on the observed rate constant when 1 equiv of crown ether was added. Kurts et al.⁸⁷ obtained results similar to ours for the kinetics of alkylation of alkali acetoacetic esters. These may be understood if the predominantly reactive species is the free enolate anion, since this ion should be unaffected by the addition of crown ethers. Since there is a reasonably large concentration of free anion, it will not be substantially increased by the addition of small amounts of complexing agents.

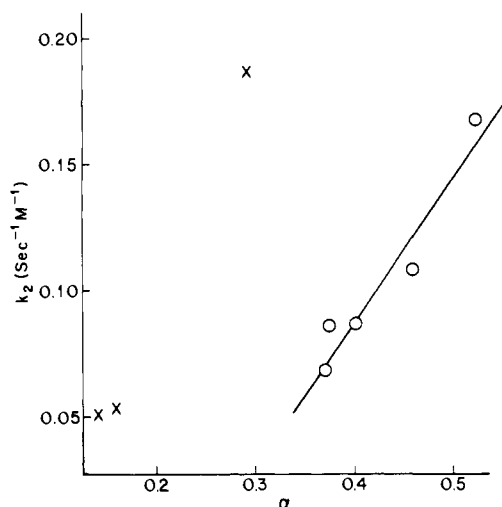


Figure 11. Plot of the calculated second-order rate constants (k_2) for the methylation of KDBM and NaDBM with dimethyl sulfate in Me_2SO vs. the degree of dissociation (α) of the enolate salt solutions.

Another plausible explanation for the insensitivity of reaction rate to the addition of complexing agents is possible. The enolate anion, with its two oxygen atoms and its negative charge, may compete effectively with the crown ether for the alkali cation. A third possibility is that the complexing agents serve only to produce externally solvated contact ion pairs. The structures of such aggregates have been proposed^{7,8} as a sandwich in which the crown ether occupies a plane above that of the enolate anion with the cation sandwiches in between them. Recently, Riche et al.⁸⁸ reported such a structure for an alkali β -keto ester-crown ether complex. These explanations are identical with those which could be proposed to account for the insensitivity of chemical shifts in both ^1H and ^{13}C NMR experiments to the addition of complexing agents.

Table XI explores the sensitivity of the system to added amounts of water. Although several studies of alkoxide ions in Me_2SO show extreme sensitivity to the presence of hydroxylic constituents, especially H_2O , the rates of methylation of the resonance stabilized β -ketoenolates considered here are not much affected by traces of water.

Oxygen Alkylation of the Enolates. Dimethyl sulfate reacts with enolates and related compounds in Me_2SO to form the oxygen alkylated product,⁸⁹⁻⁹¹ in this case the methyl vinyl ether of dibenzoylmethane, as shown by ^1H NMR. The reaction was assumed to be a simple $\text{S}_{\text{N}}2$ reaction,⁸³ and the data were analyzed as such. The results of this analysis are presented in Table XII which shows the unexpected result that the product of the observed second-order rate constant and the initial concentration of the enolate salt is approximately constant. This implies that the observed reaction is not a simple second-order reaction. Indeed, since this product is approximately constant, one could deduce that *this alkylation behaves as a first-order reaction*, its rate being approximately independent of the enolate anion concentration. A more extensive analysis of the system determined the order of the reaction with respect to the free enolate anion (0.377), the ion pair (0.235), and the total initial concentration of the enolate salt (0.234), by the van't Hoff method.

The situation is a fairly common one in mechanistic studies (e.g., halogenation of ketones, aromatic nitration) and suggests that the important rate-limiting step is the conversion of methyl sulfate to a highly reactive intermediate which reacts with enolate in a fast subsequent step. The soundness of this possibility was demonstrated by allowing a solution of dimethyl sulfate in Me_2SO to stand for 1 h before addition of NaDBM or KDBM through crushing an ampule inside the calorimeter.

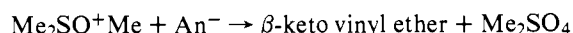
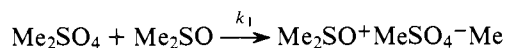
Under these conditions the reaction was instantaneous. Furthermore, ^1H NMR analysis of a mixture of dimethyl sulfate in Me_2SO showed the disappearance of DMS and the concurrent appearance of two new peaks at 4.02 and 3.44 ppm. This is indicative of the formation of dimethylmethoxysulfonium methyl sulfate, the peaks being due to the cation and anion, respectively.

The formation of a potent alkylating agent by reaction of dimethyl sulfate and Me_2SO is very strong evidence that the reactive intermediate is the dimethylmethoxysulfonium ion $(\text{Me})_2\text{SO}^+\text{Me}$ arising from oxygen alkylation of the solvent. Salts of this ion, and of its sulfur methylated isomer $(\text{Me}_3)\text{S}^+\text{O}$, have been isolated⁹²⁻⁹⁵ and their synthetic value for oxygen alkylation of ketones has been demonstrated.⁹⁶⁻⁹⁸

The fact that the oxygen methylation with Me_2SO_4 in Me_2SO is not purely zero order in enolate suggests that a second-order $\text{S}_{\text{N}}2$ attack of Me_2SO_4 on the enolate is competing with the first-order step through the dimethylmethoxysulfonium ion. The rate data were resolved by the method of Young and Andrews¹⁹ into separate rate constants for the two processes:



and



The quality of the application of this kinetic analysis to the problem may be measured by comparing the first-order rate constant (k_1) obtained thereby (Table XIII) with that ($6.81 \times 10^{-4} \text{ s}^{-1}$) obtained independently by following the rate of the reaction between Me_2SO_4 and pure Me_2SO . The agreement is quite reasonable. Failure of the two independent assessments of k_1 to match exactly is probably due to imprecision in the crude method of dissecting the kinetic data. This lack of agreement of rate constants may also be attributed to formation of the unreactive trimethylsulfoxonium salt in the reaction of dimethyl sulfate with Me_2SO . Since the rate of formation of trimethylsulfoxonium sulfate would not appear in k_1 , as determined from the dissection of rate data for enolate alkylation, the calculated k_1 should be a bit smaller, as is observed.

A control experiment with the corresponding pure *S*-methyl⁹² iodide salt showed no reaction with NaDBM over a period of 24 h. The *S*-methyl salt was readily prepared and purified according to published accounts⁹³⁻⁹⁶ and showed a sharp singlet at 3.87 ppm (in $\text{Me}_2\text{SO}-d_6$) which was not affected by prolonged contact with NaDBM.

Figure 11 is a plot of the second-order rate constant for the alkylation of potassium dibenzoylmethide by dimethyl sulfate as a function of the degree of dissociation (α). A linear correlation is obtained which confirms that the conductometrically determined free enolate anion is the reactive species. That is, in the $\text{S}_{\text{N}}2$ reaction, nucleophilic attack on the dimethyl sulfate is only performed by the free dibenzoylmethide anion. The linearity of this plot also lends credence to this mechanism of competing reactions.

To evaluate quantitatively the degree to which each mechanism contributes to the total reaction, one may compare the calculated, first-order rate constant with product of the second-order rate constant and the initial concentration of the enolate salt (see third and fourth columns of Table XIII). Both pathways contribute to a comparable extent under these conditions.

Several features of this kinetic study are instructive. First, we note the analogy between methyl transfer to solvent and

hence to the nucleophilic substrate (An^-) and the familiar proton transfer reaction through a protonated solvent molecule. In this sense the competing modes of enolate alkylation correspond crudely to proton transfer through general Brønsted acids and specific proton transfer through oxonium ion. Secondly, it is interesting to see that methyl transfer to oxygen is accomplished with high yield from alkylating agents (Me_2SO_4 or Me_2SOMe^+) in which methyl is attached to oxygen. Methyl transfer to carbon on the other hand occurs quantitatively from methyl iodide. In both cases, virtually all of the reaction may be accounted for through attack on the dissociated enolate anion.

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