residue was recrystallized from ethanol to yield the 2,4-dinitrophenylhydrazone of isobutyraldehyde (41%), mp 182–3 °C, (lit.[31] 179–86 °C).

The water layer from the ether extraction was concentrated to dryness and extracted with CHCl$_3$. Concentration of the CHCl$_3$ extracts yielded 61% of acetamide (mp 82 °C, lit.[32] 82.3 °C), whose NMR spectrum was identical with that of authentic material.

In another product study in the acidic pH region, compound **2a** (70 mg, 0.42 mmol) and benzoic acid (51 mg, 0.42 mmol, internal standard) were dissolved in 70 mL of dilute HCl to a final pH of 2.21. The final concentration of **2a** (6 mM) was comparable to that used in the kinetic studies. This solution was incubated at 60 °C for 8 h and then concentrated in vacuo. The residue was taken up in Me$_2$SO-d_6 and the acetamide singlet at δ 2.03 was integrated relative to the δ 8.0–8.3 part of the benzoic acid signal, which could be shown independently to be 36% of the total benzoic acid aromatic proton signal. (Other signals, probably due to the polymerization of the isobutyraldehyde during concentration, obscured the higher field portion of the benzoic acid signal.) The acetamide was found to be present in 106 ± 10% yield. Addition of acetic acid to the NMR tube served to show that acetamide and acetic acid singlets are clearly discernible, and therefore that the hydrolysis product is acetamide and not acetic acid. In a further control, isobutyraldehyde and benzoic acid were treated in the same manner and found not to give any interfering NMR signal in the δ 2 region.

It should be further noted that the absorbance developed in the reaction mixture as a function of time had a λ_{max} corresponding to that of authentic isobutyraldehyde.

Cyanide Trapping Experiments during the Hydrolysis of 2a. Compound **2a** (100 mg, 0.6 mmol) and NaCN (100 mg, 2.04 mmol) were heated together overnight in a phosphate buffer at 80–85 °C; the final pH of the solution was >9.0 because of the basic properties of CN$^-$. The reaction mixture was saturated with NaCl and extracted with CHCl$_3$. Concentration of the dried CHCl$_3$ extracts gave 35 mg of a liquid which was characterized as 2-amino-3-methylpropanenitrile (**6**). This identification was accomplished by spectral comparison with authentic material[33] and by hydrolysis in 6 N HCl (sealed tube, 110 °C, 21 h) to valine, which was identified by amino acid analysis. No valine was present unless the sample was first hydrolyzed. Preparations of the nitrile either during the hydrolysis of **2a** or de novo[33] always yielded material which was accompanied by a small amount of an impurity which was separated on preparative gas chromatography, and appears to be a dimer of the nitrile of as yet unidentified structure. This material does not hydrolyze to valine.

Control experiments were carried out to investigate whether the cyano amine **6** isolated from the hydrolysis of **2a** is a kinetic product of the reaction or a secondary product of de novo synthesis from isobutyraldehyde, ammonia, and cyanide. These experiments are summarized in Table VI. In a hydrolysis experiment (H1, H2, H3), 0.075–0.3 mmol (different concentrations in each experiment; an equal amount of NH$_4$Cl and 2.04 mmol of NaCN were added to 10 mL of a potassium phosphate buffer (pH 11, μ = 2.0 M (KCl)) in a serum-capped tube. The reaction tubes were incubated at 60 °C for 8 h and extracted with EtOAc (5 × 10 mL). The extracts were combined, dried (K$_2$CO$_3$), and concentrated in vacuo. An appropriate aliquot of the residue was subjected to 6 N HCl hydrolysis (110 °C, sealed tube, 22 h) and subjected to amino acid analysis. Control experiments (C1, C2, C3) were carried out in an identical manner except that isobutyraldehyde was substituted for **2a**. Valine was quantitated in an appropriate aliquot of the hydrolysate and taken as a measure of the cyanoamine **6** formed. Table VI shows that the valine found in the control is 19 ± 6% of that found in the hydrolysis.

For trapping under acidic conditions, a solution of KCN (195 mg, 3 mmol) in 5 mL of a 0.5 M acetate buffer (initially pH 4.69) was adjusted to pH 4.5 by addition of glacial acetic acid. Compound **2a** (100 mg, 0.6 mmol) was added and the reaction mixture was stirred at 60 °C for 24 h. The reaction mixture was taken to pH 10 with KOH and extracted with CHCl$_3$. The combined CHCl$_3$ extracts were washed with brine, dried, and concentrated in vacuo to yield a brown liquid (87%), identified as isobutyraldehyde cyanohydrin by comparison with an authentic sample.[34]

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Perchlorate Esters. 4. Kinetics and Mechanism of the Reactions of Alkyl Perchlorates with *N*,*N*-Dimethylanilines in Benzene[1,2]

Dennis N. Kevill* and Betty W. Shen

Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. Received December 29, 1980

Abstract: The reactions in benzene of methyl, ethyl, and isopropyl perchlorates with *N*,*N*-dimethylanilines, to yield precipitates of the quaternary anilinium perchlorate, proceed with second-order kinetics and exhibit a large negative entropy of activation. At 25.0 °C, Hammett ρ values of −3.05, −2.86, and −2.78, respectively, indicate appreciable bonding to the nitrogen within the transition state. In reaction with methyl perchlorate, the *p*-cyano and *p*-nitro derivatives require values intermediate between σ^n and σ^- and a ρ^r parameter (as defined by Young and Jencks) of −1.58 is indicated. The *p*-nitroso derivative reacts considerably faster than one would predict, and it is proposed that the nucleophilic center is the oxygen rather than the nitrogen. In reaction with *N*,*N*-dimethylaniline at 25.0 °C, comparison of methyl perchlorate with methyl-d_3 perchlorate leads to a k_H/k_D value of 0.94$_2$, and comparison with methyl iodide leads to a k_{MeOClO_3}/k_{MeI} ratio of 1170. The present results are considered together with earlier studies using methyl iodide, and mechanistic implications are discussed.

Studies of the kinetics of the Menschutkin reactions of alkyl iodides with *N*,*N*-dimethylanilines in a variety of organic solvents[3-11] have been important in the development of the Hammett equation. Because iodide is only a moderately good leaving group,[12,13] these reactions have usually been carried out at elevated

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Table I. Second-Order Rate Coefficients[a] for the Reaction of Methyl Perchlorate with 0.0418 M *N*,*N*-Dimethylaniline in Benzene at 25.0 °C

$[\mathrm{MeOClO_3}]$, *M*	0.0104	0.0208	0.0416	0.0832
$10^4 k_2$, L mol^{-1} s^{-1}	36.5	36.4	36.5	36.8

[a] Standard deviations, calculated for each run, ranged from 1 to 3% of reported value.

Table II. Second-Order Rate Coefficients[a] (L mol^{-1} s^{-1}) for the Reactions of 0.044 M Methyl, Ethyl, and Isopropyl Perchlorates with *N*,*N*-Dimethylaniline (DMA) in Benzene at 25.0 °C

[DMA], *M*	$10^4 k_2^{\mathrm{Me}}$	$10^4 k_2^{\mathrm{Et}}$	$10^4 k_2^{i\text{-}\mathrm{Pr}}$
0.0105	34.4	2.13[b]	0.90
0.0209	35.5	2.21	
0.0418	36.5	2.35	0.94
0.0625	38.5	2.45	0.95[c]
0.0858	38.8	2.63	0.96
0.125	40.3	2.55	0.96[d]
0.169	41.0[e]	2.68[f]	1.01

[a] For methyl and ethyl perchlorates, standard deviations range from 1 to 5% of reported value and, for isopropyl perchlorate (initial values obtained by extrapolation of a plot vs. extent of reaction), from 3 to 10% of reported value. [b] Standard deviation (±0.29) unusually high. [c] [DMA] = 0.0674 M. [d] [DMA] = 0.135 M. [e] [DMA] = 0.162 M. [f] [DMA] = 0.176 M.

Table III. Extrapolated Second-Order Rate Coefficients[a, b] (L mol^{-1} s^{-1}) and Calculated Enthalpies and Entropies of Activation[c] for the Reactions of Alkyl Perchlorates with *N*,*N*-Dimethylaniline in Benzene

temp, °C	$10^4 (k_2^{\circ})^{\mathrm{Me}}$	$10^4 (k_2^{\circ})^{\mathrm{Et}}$	$10^4 (k_2^{\circ})^{i\text{-}\mathrm{Pr}}$
15.7	20.3	0.99	0.252
25.0	34.4	2.16	0.91
33.5	69.3	4.46	2.09
44.2	107.1	8.90	3.56
54.4	214.6	18.32	7.98
$\Delta H^{\ddagger}_{298}$, kcal mol^{-1}	11.2 ± 0.3	12.9 ± 0.2	14.2 ± 0.2
$\Delta S^{\ddagger}_{298}$, cal K^{-1} mol^{-1}	−34.9 ± 1.1	−34.4 ± 0.8	−32.0 ± 0.7

[a] Extrapolated to infinitely low concentration of amine. [b] Standard deviations ranged from 0.3 to 3% of reported values. [c] With associated standard deviations and calculated from the values for the extrapolated second-order rate coefficients.

Table IV. Effect of Added Tetra-*n*-butylammonium Perchlorate upon the Second-Order Rate Coefficients[a] for Reaction of 0.042 M Methyl Perchlorate with 0.084 M *N*,*N*-Dimethylaniline in Benzene at 25.0 °C

10^2-[n-$\mathrm{Bu_4NClO_4}$]	0.000	0.125	0.250	0.500	1.000	2.000
$10^4 k_2$, L mol^{-1} s^{-1}	38.8	42.5	42.9	44.4	47.1	47.9

[a] Standard deviations, calculated for each run, in the range of 2 to 3% of the reported value.

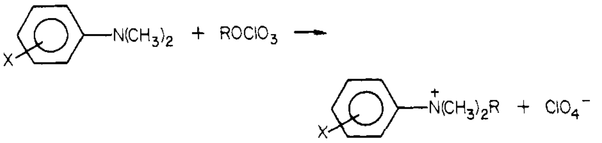
Table V. Deuterium Isotope Effect upon the Second-Order Rate Coefficients for Reaction of Methyl Perchlorate (k_2^{H}, L mol^{-1} s^{-1}) or Methyl-d_3 Perchlorate (k_2^{D}, L mol^{-1} s^{-1}) with *N*,*N*-Dimethylaniline (DMA) in Benzene at 25.0 °C

[DMA]	$10^3 k_2^{\mathrm{H}\,a}$	$10^3 k_2^{\mathrm{D}\,a}$	$k_2^{\mathrm{H}}/k_2^{\mathrm{D}\,a,b}$
	Series A[c]		
0.2007	4.01 ± 0.16	4.29 ± 0.20	0.938 ± 0.016
0.1605	3.95 ± 0.06	4.24 ± 0.11	0.931 ± 0.017
0.1003	3.83 ± 0.18	4.08 ± 0.05	0.938 ± 0.014
0.0803	3.80 ± 0.04	4.09 ± 0.09	0.938 ± 0.009
	Series B[d]		
0.1600	3.98 ± 0.04	4.24 ± 0.09	0.935 ± 0.019
0.1280	3.86 ± 0.04	4.13 ± 0.04	0.929 ± 0.013
0.0800	3.86 ± 0.04	4.05 ± 0.06	0.953 ± 0,007
0.0640	3.83 ± 0.03	4.07 ± 0.03	0.942 ± 0.006
0.0400	3.75 ± 0.10	4.03 ± 0.05	0.933 ± 0.022

[a] With associated standard deviations. [b] Calculated, for each run, on a point by point basis and averaged. [c] With 0.03472 M $\mathrm{CH_3OClO_3}$ or 0.03650 M $\mathrm{CH_3OClO_3}$-d_3. [d] With 0.04139 M $\mathrm{CH_3OClO_3}$ or 0.04014 M $\mathrm{CH_3OClO_3}$-d_3.

temperatures. Iodide is a good nucelophile,[14] especially in aprotic solvents,[15] and reversibility has been a major problem, especially in the presence of strongly electron-withdrawing substituents within the aromatic ring of the amine. For alkyl iodides other than methyl, the reverse reaction is accompanied by transalkylation.[10] The perchlorate ion has high nucleofugality[12,16] and low nucleophilicity,[14] and Menschutkin-type reactions proceed smoothly to completion, at temperatures close to ambident, even in the presence of strongly electron-withdrawing substituents within the amine.

A report follows of the observed kinetic patterns, activation parameters, and Hammett correlations[17] for the quaternizations of *N*,*N*-dimethylaniline with methyl, ethyl, and isopropyl perchlorates in benzene (eq 1). With methyl perchlorate the effect



(1)

of added common-ion salt and the α-deuterium isotope effect have also been investigated.

Experimental Results

Unless otherwise stated, reactions were in benzene at 25.0 °C. With the exception of reactions involving *p*-nitroso-*N*,*N*-dimethylaniline, a crystalline precipitate of the predicted quaternary ammonium perchlorate separated from solution.

Kinetics of Reactions with *N*,*N*-Dimethylaniline. For reaction of a constant *N*,*N*-dimethylaniline concentration with 0.01–0.08 M methyl perchlorate, the second-order rate coefficients were shown to be essentially constant (Table I). For reaction of a constant methyl or ethyl perchlorate concentration with 0.01–0.17 M *N*,*N*-dimethylaniline, constant values for the second-order rate coefficient were obtained throughout each individual run, but the averaged values obtained for each run increased with increasing initial amine concentration (Table II). For the corresponding reaction of a constant concentration of isopropyl perchlorate, the values for the integrated second-order rate coefficients increased throughout each individual run and a plot of these values vs. extent of reaction is essentially linear. Initial values were obtained by extrapolation of these plots and these initial values also increased with increasing initial amine concentration (Table II). A 0.04 M solution of 2-adamantyl perchlorate did not react with 0.16 M *N*,*N*-dimethylaniline over a period of 2 months.

Studies were made at several temperatures and the averaged (methyl and ethyl perchlorates) or initial (isopropyl perchlorate) second-order rate coefficients (k_2) gave, at each temperature, a linear plot when plotted against the initial amine (DMA) concentration. This can be expressed as eq 2, where k_2^0 is the second-order rate coefficient value corresponding to a very low [DMA] and, at a given temperature, b is a constant. The k_2^0 values, together with the calculated enthalpies and entropies of activation, are given in Table III.

$$k_2 = k_2^0(1 + b[\mathrm{DMA}]) \qquad (2)$$

The effect of added tetra-*n*-butylammonium perchlorate to a constant concentration of both methyl perchlorate and *N*,*N*-dimethylaniline was quite modest. A less than linear increase in rate with increasing salt concentration was observed (Table IV).

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Table VI. Second-Order Rate Coefficients[a] for the Reaction of 0.04 M Alkyl Perchlorates ($ROClO_3$) with Ring-Substituted *N,N*-Dimethylanilines ($XC_6H_4NMe_2$) in Benzene at 25.0 °C

X = *p*-CH_3O ($\sigma = -0.268$)[b]; R = Me							
10^2[amine]	1.29	2.55	6.48	7.76	12.95	16.90	
10^2k_2 (L mol^{-1} s^{-1})	3.25	3.29	3.35	3.24	3.56	3.82	
X = *p*-CH_3 ($\sigma = -0.170$); R = Me							
10^2[amine]	2.16	4.31	6.89	8.62	13.79	16.55	
10^2k_2 (L mol^{-1} s^{-1})	1.09	1.16	1.16	1.19	1.19	1.19	
X = *m*-CH_3 ($\sigma = -0.069$); R = Me							
10^2[amine]	1.05	2.09	4.19	6.60	8.38	13.20	16.75
10^3k_2 (L mol^{-1} s^{-1})	6.01	6.11	6.22	6.32	6.26	6.35	6.49
X = *p*-Br ($\sigma = +0.232$); R = Me							
10^2[amine]	1.06	2.12	4.24	6.42	8.48	12.84	15.72
10^4k_2 (L mol^{-1} s^{-1})	6.32	6.21	6.39	6.93	6.93	7.57	7.51
X = *m*-Cl ($\sigma = +0.373$); R = Me							
10^2[amine]	2.01	4.01	6.41	8.02	12.83	16.04	
10^4k_2 (L mol^{-1} s^{-1})	2.81	2.80	3.06	3.16	3.24	3.35	
X = *m*-NO_2 ($\sigma = +0.710$); R = Me							
10^2[amine]	1.59	3.19	5.73	7.92	11.45	12.78	15.83
10^5k_2 (L mol^{-1} s^{-1})	2.95	3.19	3.43	3.63	3.82	3.99	4.19
X = *p*-CN ($\sigma = +0.628$; $\sigma^- = +1.00$[d]); R = Me							
10^2[amine]	1.02	2.04	4.09	6.54	8.18	13.08	15.60
10^5k_2 (L mol^{-1} s^{-1})	0.93	1.07	1.18	1.26	1.32	1.53	1.68
X = *p*-NO_2[c] ($\sigma = +0.778$; $\sigma^- = +1.27$[d]); R = Me							
10^2[amine]	2.44	4.89	7.07				
10^6k_2 (L mol^{-1} s^{-1})	2.72	3.04	3.34				
X = *p*-NO ($\sigma = +0.123?$); R = Me							
10^2[amine]	4.13	8.25	16.5				
10^3k_2 (L mol^{-1} s^{-1})	5.30	5.69	6.58				
X = *p*-CH_3; R = Et							
10^2[amine]	1.00	2.00	4.01	6.42	8.03	12.83	16.04
10^4k_2 (L mol^{-1} s^{-1})	6.84	7.21	7.33	7.36	7.36	7.66	7.97
X = *m*-CH_3; R = Et							
10^2[amine]	1.00	2.01	4.02	6.43	8.04	12.86	16.08
10^4k_2 (L mol^{-1} s^{-1})	3.38	3.49	3.48	3.49	3.58	3.61	3.67
X = *m*-Cl; R = Et							
10^2[amine]	1.12	2.24	4.48	6.40	8.00	12.80	16.01
10^5k_2 (L mol^{-1} s^{-1})	1.92	1.99	1.99	2.08	2.06	2.32	2.23
X = *p*-CH_3; R = *i*-Pr							
10^2[amine]	1.99	3.98	6.37	7.96	12.74	15.93	
10^4k_2 (L mol^{-1} s^{-1})[e]	2.93	3.09	2.91	3.02	3.18	3.25	
X = *m*-CH_3; R = *i*-Pr							
10^2[amine]	1.02	2.05	4.09	6.43	8.04	12.86	16.08
10^4k_2 (L mol^{-1} s^{-1})[e]	1.48	1.61	1.63	1.50	1.57	1.68	1.74
X = *m*-Cl; R = *i*-Pr							
10^2[amine]	2.29	4.58	6.16	8.09	12.94	16.18	
10^6k_2 (L mol^{-1} s^{-1})[e]	8.81	9.42	9.58	9.58	10.25	10.49	

[a] Standard deviations, calculated for each run, range from 1 to 6% of reported values. [b] Hammett σ values from ref 17. [c] Concentration range limited by the low solubility of this amine. [d] Value recommended for use in reactions of phenols and anilines. [e] Initial values obtained by extrapolation of a plot vs. extent of reaction.

Kinetic Deuterium Isotope Effects in the Reaction of Methyl Perchlorate with *N,N*-Dimethylaniline. With the concentration of methyl perchlorate or methyl-d_3 perchlorate at ca. 0.04 M, two series of runs were carried out with varying (0.04–0.20 M) concentrations of *N,N*-dimethylaniline. Averaged values for the integrated second-order rate coefficients are reported in Table V, together with the values obtained for the deuterium isotope effect (k_2^H/k_2^D). To mimimize errors the runs with undeuterated and deuterated ester were carried out side by side and portions simultaneously removed for analysis. The k_2^H/k_2^D values were calculated on a point-by-point basis and the nine values obtained for each run were averaged; no trend with amine concentration was discernible and the k_2^H/k_2^D values of Table V were averaged, with weighting inversely proportional to the squares of the associated standard deviations, to give a k_2^H/k_2^D value of 0.9424 ± 0.0024 (standard error).

Effect of Ring Substitution within the *N,N*-Dimethylaniline. For reaction with methyl perchlorate, second-order rate coefficients have been determined for nine meta- and para-substituted derivatives of *N,N*-dimethylaniline. Amine concentrations were usually ≤0.17 M but solubility considerations limited the study with the *p*-nitro derivative to ≤0.07 M. The mean values obtained are reported in Table VI. For reaction with ethyl and isopropyl perchlorates, a study was carried out with *p*-CH_3, *m*-CH_3, and *m*-Cl derivatives. The averaged second-order rate coefficient values for ethyl perchlorate and the initial values for isopropyl perchlorate are also reported in Table VI.

Analysis paralleling that carried out for the unsubstituted *N,N*-dimethylaniline (Table III) led to values for k_2^0 and *b*, as defined in eq 2, and these values are reported in Table VII.

Product Studies. The reaction of methyl perchlorate with *p*-nitroso-*N,N*-dimethylaniline proceeded with formation of unidentified black tars. All other reactions proceeded with precipitation of crystalline quaternary ammonium perchlorates. After in excess of 10 half-lives at ca. 22 °C, the precipitates were removed by filtration and washed with benzene. Details of illustrative experiments are given in the Experimental Section.

For reactions of 0.05–0.15 M *N,N*-dimethylaniline (or a substituted derivative) with 0.04 M methyl perchlorate the isolated yields of analytically pure salt were in the range of 91–99%, with an average value for the nine systems studied at 96%. For 0.076 M ethyl perchlorate in reaction with 0.12 to 0.18 M unsubstituted or ring-substituted *N,N*-dimethylaniline, the isolated yields of analytically pure salt ranged from 92 to 99%, with an average value for the four systems studied at 96%.

The benzene solution of isopropyl perchlorate was contaminated with 4–7% acid and one would, therefore, expect the precipitated quaternary anilinium perchlorate to be contaminated with *N,N*-dimethylanilinium perchlorate. While it has been assumed that reactions of isopropyl iodide with pyridine[18] or triethylamine[19]

Table VII. Extrapolated Second-Order Rate Coefficients and *b* Values[a] for the Reactions between Alkyl Perchlorates ($ROClO_3$) and *N*,*N*-Dimethylanilines ($XC_6H_4NMe_2$) in Benzene at 25.0 °C

R	X	k_2^0 (L mol^{-1} s^{-1})[b]	*b* (L mol^{-1})[b]
CH_3	*p*-CH_3O	3.01 (±0.04) × 10^{-2}	1.46 ± 0.04
	p-CH_3	1.12 (±0.05) × 10^{-2}	0.43 ± 0.02
	m-CH_3	6.00 (±0.10) × 10^{-3}	0.45 ± 0.06
	H	3.44 (±0.08) × 10^{-3}	1.43 ± 0.10
	p-Br	6.12 (±0.24) × 10^{-4}	1.60 ± 0.16
	m-Cl	2.66 (±0.05) × 10^{-4}	1.44 ± 0.19
	m-NO_2	2.86 (±0.16) × 10^{-5}	3.16 ± 0.22
	p-CN[c]	9.46 (±0.54) × 10^{-6}	4.93 ± 0.19
	p-NO_2[c]	2.41 (±0.02) × 10^{-6}	5.39 ± 0.91
	p-NO[c]	4.85 (±0.04) × 10^{-3}	2.14 ± 0.07
Et	*p*-CH_3	6.97 (±0.18) × 10^{-4}	0.86 ± 0.09
	m-CH_3	3.39 (±0.07) × 10^{-4}	0.52 ± 0.09
	H	2.16 (±0.14) × 10^{-4}	1.57 ± 0.26
	m-Cl	1.90 (±0.09) × 10^{-5}	1.28 ± 0.20
i-Pr	*p*-CH_3	2.89 (±0.13) × 10^{-4}	0.74 ± 0.10
	m-CH_3	1.55 (±0.10) × 10^{-4}	0.62 ± 0.01
	H	9.08 (±0.02) × 10^{-5}	0.56 ± 0.10
	m-Cl	8.76 (±0.02) × 10^{-6}	1.27 ± 0.10

[a] Calculated using the equation $k_2 = k_2^0(1 + b[\text{amine}])$ and the second-order rate coefficients reported in Tables II and VI.
[b] With associated standard deviations. [c] Data not included in the calculation of the Hammett ρ value.

in benzene lead only to the quaternary ammonium compound, elimination to propylene plus *N*,*N*-dimethylanilinium perchlorate could, in principle, accompany the substitution. Reaction of 0.100 M isopropyl perchlorate (contaminated with 0.006 M acid) with 0.077 M *m*-methyl-*N*,*N*-dimethylaniline led to a 98% crude isolated yield (based on formation of the quaternary anilinium compound). After recrystallization from acetone, a 80% yield of analytically pure *m*-methyl-*N*-isopropyl-*N*,*N*-dimethylanilinium perchlorate was obtained. The precipitate formed from the reaction of 0.035 M isopropyl perchlorate (contaminated with 0.002 M acid) with 0.058 M *N*,*N*-dimethylaniline was shown by a PMR study in acetonitrile-d_3 to contain 6 mol % *N*,*N*-dimethylanilinium perchlorate and 94 mol % *N*-isopropyl-*N*,*N*-dimethylanilinium perchlorate.

Discussion

The reactions of methyl and ethyl perchlorates proceed with essentially quantitative (ca. 96%) precipitation of the analytically pure quaternary ammonium perchlorates. With isopropyl perchlorate, the small percentage of contaminant acid is carried over into the precipitate but crude yields of 98% and recrystallized, analytically pure yields of 80% could be obtained. It appears that, as previously assumed,[18,19] isopropyl derivatives undergo Menschutkin reactions with little, if any, accompanying elimination.

For the reactions of methyl and ethyl perchlorates good integrated second-order rate coefficients were obtained throughout each individual run, but for isopropyl perchlorate the values rose linearly with the extent of reaction and initial values were obtained by extrapolation. Autocatalysis is not uncommon in Menschutkin reactions and, indeed, Laidler and Hinshelwood[19] in studying reaction with a benzene solution of triethylamine observed autocatalysis for isopropyl iodide but not for methyl iodide, paralleling our observations with the perchlorate esters. They ascribed the difference in behavior to an increased solubility, and hence an increased medium effect, when the nitrogen of the cation bears an isopropyl as opposed to a methyl group. However, in a study using substituted *N*,*N*-dimethylanilines in a variety of solvents, Rossell[10] observed autocatalysis only in some (but not all) of the instances where precipitation was observed, and he concluded that a surface effect was involved. The latter explanation seems more probable because we observe for isopropyl perchlorate that the rate coefficients continue to increase in value throughout the reaction but the solution becomes saturated with the formed salt at a very early stage. In benzene, the relative rates of homogeneous and heterogeneous Menschutkin reactions must be delicately balanced and very sensitive to the nature of the alkyl group involved.

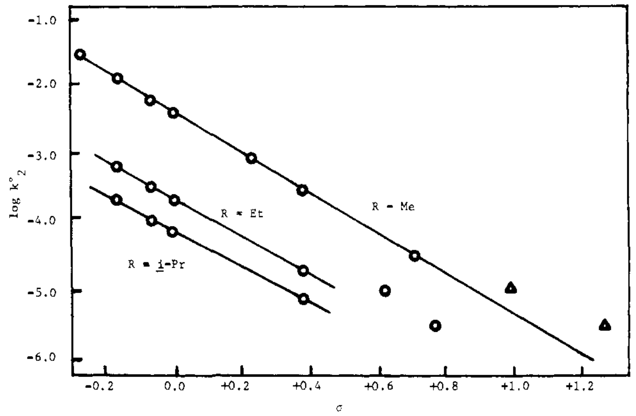

Figure 1. Hammett plots for the reactions of perchlorate esters (RO-ClO_3) with para- and meta-substituted *N*,*N*-dimethylanilines in benzene at 25 °C. Substituents occur in the order (based on decreasing k_2^0 values) that they appear in Table VII. Triangles represent points based upon σ^- values.

The approximately linear increase in the value for the second-order rate coefficient with increasing initial amine concentration (Table II) could be expressed in terms of concurrent second- and third-order processes, but the increases, expressed as *b* values (Table VII), do not correlate with the Hammett σ values for the substituent. The *b* values do show a general trend toward larger values for the more polar substituents, and they are probably best explained as medium effects upon a reaction going from uncharged reactants to a charged transition state. The values of the second-order rate coefficient used in treatment of temperature and substituent effects are initial values obtained by use of eq 2.

The second-order rate coefficients fall in value: Me > Et > *i*-Pr ≫ 2-Ad. Under bimolecular conditions, 2-adamantyl derivatives are known to be very unreactive owing to steric hindrance exhibited by the axial hydrogen atoms on the tetrahedral faces of adamantane.[20] The activation parameters (Table III) are also consistent with a S_N2 mechanism. The large negative entropies of activation[21] and the increases in enthalpies of activation[10,19] as one goes from Me → Et → *i*-Pr are in accord with previous observations concerning Menschutkin reactions.

Consistent with the charge type of the reaction, it is accelerated by added inert salt. Tetra-*n*-butylammonium perchlorate produces modest rate increases (Table IV) and the increases are less than linearly related to the salt concentration. The initial slope corresponds to a *b* value in $k_2 = k_2^0(1 + b[\text{salt}])$ of approximately 100, a reasonable value for a reaction of this charge type in a low polarity solvent in the absence of any specific interactions.

The small inverse deuterium isotope effect of 0.94_2 for reaction of methyl perchlorate with *N*,*N*-dimethylaniline (Table V) is for a reaction which would be classified by Gray, Coward, Schowen, and Schowen[22] as M-2,2. The value is well within the range of values they have assembled for S_N2 reactions of this type. The value of 0.92_4 (at 23.1 °C) for the hydrolysis of methyl perchlorate[23] should also be added to their compilation.

For the reaction of *N*,*N*-dimethylaniline with methyl perchlorate, a thorough study has been carried out of the effect upon the second-order rate coefficients of the introduction of meta and para substituents (Table VI). The coefficients were analyzed using

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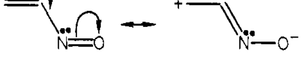
eq 2 to obtain the k_2^0 and b values reported in Table VII. Using the k_2^0 values, a Hammett plot has been constructed[17] (Figure 1). Since the *p*-nitroso derivative led to black tars and not the crystalline solids obtained in all other cases, the point for its reaction was omitted from the plot.

A linear plot ($\rho = -3.05 \pm 0.06$) was obtained providing the points for *p*-nitro and *p*-cyano derivatives were neglected. Use of the σ^- values for these two derivatives, allowing for direct conjugation with the reaction center (recommended for use especially with phenols and anilines[17]), resulted in overcompensation. The requirement of values intermediate between the (inductive) σ^n and the σ^- values is quite common, and it has been considered by Yukawa and Tsuno[24] and more recently by Young and Jencks.[25] A linear free energy relationship of the form shown in eq 3 can

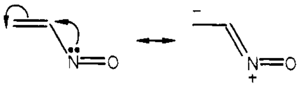
$$\log (k/k^0) = \rho(a\sigma_I + b\sigma_R) \qquad (3)$$

be written where $a + b = 1$ and the magnitudes of a and b are determined by the relative amounts of electron withdrawal by induction and resonance. Using values[26] for the *p*-cyano derivative of +0.674 for σ_I and +1.00 for σ_R and for the *p*-nitro derivative of +0.778 for σ_I and +1.27 for σ_R, a values can be calculated as 0.49 and 0.48, respectively. Alternatively, analysis as suggested by Young and Jencks[25] leads to a value for the ρ^r (resonance effect) parameter of −1.58. On reflection, it is perhaps fortunate that pioneer workers,[3,7] because of slow reactions and unfavorable equilibria, were unable to obtain rates for the *p*-nitro derivative in Hammett equation studies of Menschutkin reactions with alkyl iodides.

The second-order rate coefficients for reaction with *p*-nitroso-*N*,*N*-dimethylaniline at 25.0 °C extrapolate to a k_2^0 value of 4.85×10^{-3} L mol^{-1} s^{-1}, compared to a value of 3.44×10^{-3} L mol^{-1} s^{-1} in the absence of substituent (Table VII). Using the calculated ρ value of −3.05, a σ value for the *p*-nitroso substituent of −0.050 is indicated. Jaffé, using the data of Davies and Addis[27] for the equilibrium protonation of *N*,*N*-dimethylanilines in 50% aqueous ethanol at 20 °C, has reported[17] a value of +0.123. Rossell[10] included the *p*-nitroso derivative in his kinetic study of the reactions of *N*,*N*-dimethylanilines with ethyl iodide in nitrobenzene. At 25.0 °C, using a calculated ρ value of −3.60, a σ value of −0.068 is obtained, at 60 °C the values are −3.20 and −0.114, and at 80 °C the values are −2.91 and −0.121. The σ value from the present study, the Jaffé value, and the values calculated from the Rossell data are all fairly close to zero. However, Ranganathan, Singh, and Panda,[28] on the basis of HMO calculations, have suggested that, in α,β-unsaturated nitroso systems, a contribution of the type



is extremely important, and a contribution of the type



is much less important. This suggests that a *p*-nitroso substituent capable of conjugation with an unsaturated π system should be a powerful electron-withdrawing group, and the $\sigma_{p\text{-NO}}$ value should be fairly large and positive; support comes from ^{19}F NMR studies of fluorobenzenes[29,30] and a σ_p^0 value for *p*-nitroso (from the sum of inductive and resonance values) of +0.65 can be obtained.[31] Parallel calculation for *p*-nitro leads to a value of +0.76, in excellent agreement with the traditional value, and an appreciable degree of confidence can be placed in this approach. It is probable that the discrepancy for the values from protonation or alkylation studies using *N*,*N*-dimethylanilines is due to reaction occurring at the oxygen of the nitroso group and not the nitrogen of the amino group. Support for appreciable nucelophilicity at a *p*-nitroso oxygen comes from the observation of intramolecular neighboring group participation in the acetolysis of suitably substituted primary *p*-toluenesulfonates.[32]

Table VIII. Calculated Hammett ρ Values Based upon the Second-Order Rate Coefficients for the Reactions of Methyl Iodide with Substituted *N*,*N*-Dimethylanilines in Various Solvents[a,b]

	temperature, °C			
solvent	30	40	50	60
C_6H_6		−3.28[c]		
THF[d]		−3.00		
$C_6H_5NO_2$	−2.97	−2.86	−2.74	−2.60[e]
$(CH_3)_2CO$	−2.56[f]	−2.43	−2.39	−2.25
CH_3CN	−2.56	−2.53	−2.44	−2.39
CH_3OH		−2.44[g]	−2.40[g]	*h*

[a] Using, except where otherwise indicated, data for *N*,*N*-dimethylaniline and the *p*-CH_3, *m*-CH_3, and *m*-Cl derivatives. [b] Using rate coefficients from ref 11. [c] Data not available for *m*-Cl derivative. [d] Tetrahydrofuran. [e] Data not available for the unsubstituted compound. [f] Neglecting an apparently erroneous value for the *p*-methoxy derivative and based on *N*,*N*-dimethylaniline plus seven commonly used derivatives, a value from ref 8 of −2.42 at 35 °C can be calculated. [g] Data not available for the *p*-CH_3 derivative. [h] From data in ref 7, a value of −2.14 at 65 °C has been calculated (ref 17).

Matsui and Tokura[11] have measured the second-order rate coefficients for reaction of methyl iodide with 0.08 M *N*,*N*-dimethylaniline in benzene at 30, 40, and 50 °C. From these data a value of 3.3×10^{-6} L mol^{-1} s^{-1} at 25.0 °C can be calculated. For reaction of methyl perchlorate, the corresponding value is 3.86×10^{-3} L mol^{-1} s^{-1} and methyl perchlorate reacts, under these conditions, 1170 times as rapidly as methyl iodide. In addition to the parent compound, the *p*- and *m*-methyl derivatives were also studied[11] in the reaction with methyl iodide at 40 °C. Although the range of σ values is rather narrow, an approximate ρ value of −3.28 can be calculated. Based on the temperature variation of the corresponding ρ values in acetone, acetonitrile, and nitrobenzene (Table VIII), a value of approximately −3.4 would be predicted for a study at 25 °C. This value is only slightly larger than our corresponding value for methyl perchlorate of −3.05 and it provides for S_N2 reactions a further example of the insensitivity of substituent effects within the attacking nucleophile to wide variations in leaving-group ability.[1,33,34]

With methyl perchlorate, the low nucleophilicity of perchlorate ion prevents any appreciable reversal of reaction even in the presence of the more powerfully electron-withdrawing substituents within the amine. For the earlier studied alkyl iodides, reversibility frequently presented a major problem and Rossell[10] and Matsui and Tokura[11] attempted to correct for movement toward an equilibrium in their calculation of second-order rate coefficients. A major difficulty was presented by the uncertainty as to the relative extents to which ion pairs and free ions are involved in the reverse reaction.[35] The two reports sometimes differ appreciably in the corrected values obtained; for example, in nitrobenzene at 40 °C, the rate coefficients for reaction of the *m*-nitro derivative with methyl iodide differ by about 50%. This appears to result from difficulties in the kinetic analysis rather

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than from the use of solvent samples of different purity, since their corresponding results for the *m*-methyl derivative, where reversal does not present a problem, differ by less than 5%. In considering these results,[10,11] we have omitted from the analyses values relating to the *m*-nitro derivative.

Rossell[10] reported a Hammett ρ value for the reaction of methyl iodide with *N,N*-dimethylanilines in nitrobenzene at 80 °C of −2.29, but recalculation with omission of the dubious *m*-nitro point changes this value to −2.75. This recalculated value is virtually identical with the value of −2.85 reported for ethyl iodide.[36a] However, the slightly more negative value for ethyl iodide does appear to be meaningful since calculations (omitting the *m*-nitro value when available) give corresponding values at 25 °C of −3.09 and −3.60, at 40 °C of −3.10 and −3.32, and at 60 °C of −2.90 and −3.20.

Our values at 25 °C for reaction with alkyl perchlorates in benzene are -3.05 ± 0.06 ($n = 7$) for methyl perchlorate, -2.86 ± 0.03 ($n = 4$) for ethyl perchlorate, and -2.78 ± 0.05 ($n = 4$) for isopropyl perchlorate (see Figure 1). Analysis of the methyl perchlorate data, limiting to the same derivatives as for the ethyl and isopropyl perchlorates, leads to a value of -3.01 ± 0.06 ($n = 4$). It is tempting to consider a rationalization within which formation of a looser transition state as one goes from methyl to ethyl to isopropyl perchlorate involves reduced bonding to the nitrogen and less negative ρ values. However, the data obtained by Rossell[10] for reaction in nitrobenzene indicates, within the temperature range of 25–80 °C, ethyl iodide to have a *more* negative ρ value than methyl iodide. The difference between the ρ values obtained from the Rossell study gets smaller with increasing temperature and one would expect a crossover at a temperature not considerably in excess of 80 °C; it is quite possible that the opposite ordering of the ρ values for methyl and ethyl perchlorates in benzene results not from any fundamental difference in mechanism but from a crossover here coming at a temperature of less than the 25 °C at which the comparison is made.[36b] This discussion illustrates very well a major consideration in interpreting small differences between ρ values in terms of mechanism: a quite modest temperature variation might well lead to an inversion of the magnitudes of the ρ values for the two systems.

While reversibility poses a problem in accurate measurement of rate coefficients with methyl iodide as substrate, it does (in principle at least) allow a comparison of kinetic and equilibrium ρ values. The values available for equilibrium constants can only be considered as approximate[35] but, in nitrobenzene at 60 °C, the equilibrium ρ values calculated from the data of Rossell[10] (−3.55, $r = 0.999$, $n = 3$) and, excluding the very approximate *p*-methyl value, the data of Matsui and Tokura[11] (−3.78, $r = 0.991$, $n = 4$) are in reasonable agreement. The corresponding kinetic ρ values are −2.90 ($r = 0.999$, $n = 3$) and −2.60 ($r = 0.999$, $n = 3$), respectively; based on data of Laidler[5] a value of −2.71 ($r = 0.996$, $n = 5$) had previously been reported.[17] The kinetic ρ value is therefore about 75% of the equilibrium ρ value, suggesting considerable bonding of the amine to the methyl carbon in the transition state. Abraham[35,37,38] has estimated that, in reactions of trialkylamines with methyl iodide, there is 40% charge separation between the nitrogen and the iodine. It is, however, not required that the ρ value should be linearly related to the extent of charge separation.[39] Both approaches suggest that the reaction resembles a classical S_N2 reaction rather than the S_N2C^+ reaction[40] proposed by Sneen[41] and, subsequently, suggested even for bimolecular nucelophilic substitution reactions of methyl derivatives.[23,42,43] Similar conclusions have been reached from consideration of the reactions of meta- and para-substituted arenesulfonate ions with powerful methylating agents in acetonitrile.[1,44,45] Systematic variation within the nucleophile is probably the most sensitive of the simple probes available for these systems. Reactivity–selectivity considerations and the Hammond postulate would require[44] low selectivity (low ρ values) for those situations where attack was upon an extremely reactive preformed intermediate carbenium ion,[46] and ρ values constituting an appreciable fraction of the equilibrium ρ value are more consistent with a classical S_N2 mechanism.

Experimental Section

Materials. The *p*-methoxy-*N,N*-dimethylaniline was prepared from *p*-anisidine and methyl iodide following the procedure of Davies.[47] Tetra-*n*-butylammonium perchlorate was recrystallized from acetone and dried overnight at 60–80 °C under reduced pressure. Methyl, ethyl, and isopropyl iodides were fractionally distilled from a drop of mercury and the 1- and 2-adamantyl bromides were recrystallized from methanol. Silver perchlorate was dried to constant weight at 120 °C. Benzene (Fisher, reagent grade) was refluxed with sodium metal for 24 h, distilled through a 45-cm fractionating column, and passed through a column of Linde 4A molecular sieves.

Alkyl Perchlorate Solutions. The appropriate alkyl halide was reacted with silver perchlorate as previously reported,[48] with the modification that homogeneous reaction in benzene[49] was used. After removal of silver halide by filtration, the filtrate (ca. 0.2 M in perchlorate ester) was passed through a short column of Linde 4A molecular sieves. The extent of contaminant acid was determined by addition of a portion to acetone at −78 °C and titration against sodium ethoxide in ethanol to a Resorcinol Blue (Lacmoid) end point. Acid was absent in the methyl, ethyl, and 2-adamantyl perchlorate solutions and was present to the extent of about 6% in the isopropyl perchlorate solutions. Reaction of 1-adamantyl bromide did not lead to perchlorate ester and, on concentration of the filtrate, a white precipitate of 1-adamantylbenzene separated, mp 81.2–82.8 °C (lit.[50] mp 82 °C).

Since alkyl perchlorates are extremely explosive,[48,51] no isolation was attempted, and the exact concentrations of the benzene solutions were determined by addition of a portion to excess sodium ethoxide in ethanol and, after 4 h, back-titration with a standardized solution of HCl in methanol. The yields within solution were 92% for methyl perchlorate, 89% for ethyl perchlorate, 80% for isopropyl perchlorate (after correction for the 6% contaminant acid), and 93% for 2-adamantyl perchlorate.

Kinetic Procedures. Reaction solutions (25 mL) were made up from the appropriate perchlorate ester solution, a stock solution (usually 0.2 M) in benzene of the required amine, and benzene, all contained within the constant-temperature water bath. After a short time interval for reequilibration, a 2-mL portion was removed and the concentration of perchlorate ester at this arbitrary time zero determined by addition to a known (and excess) amount of sodium ethoxide in ethanol (10 mL). After 20 min for $MeOClO_3$, 40 min for $EtOClO_3$, or 4 h for *i*-$PrOClO_3$ or 2-$AdOClO_3$, the excess amount of NaOEt was determined by back-titration against HCl in MeOH to a Resorcinol Blue (Lacmoid) end point. Further 2-mL portions were removed at suitable time intervals (avoiding precipitate) and analyzed in the same manner. Second-order rate coefficients were calculated from the standard form of the integrated rate equation.

A benzene solution 0.0372 M in 2-adamantyl perchlorate and 0.16 M in *N,N*-dimethylaniline showed no precipitation and no change in ester concentration throughout a period of 2 months at 25.0 °C.

Product Studies. Reactions of methyl, ethyl, and isopropyl perchlorates (0.04–0.08 M) with an excess amount of amine (0.05–0.18 M) in benzene were allowed to go to completion at room temperature. Reaction times were typically 2 weeks but ranged up to 3 months in the presence of strongly electron-withdrawing substituents within the amine.

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(36) (a) Omission of the *m*-NO_2 derivative point for ethyl iodide changes this value only to −2.91, suggesting that the reported rate coefficient value is here quite accurate. (b) For a discussion of the temperature dependence of selectivity values, see Giese, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 125.

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(43) See, however (a) McLennan, D. J. *Acc. Chem. Res.* **1976**, *9*, 281. (b) Abraham, M. H.; McLennan, D. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 873.

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The reaction mixtures were filtered and the precipitated quaternary anilinium perchlorates were washed twice with benzene. Frequently these products were of analytical purity. When necessary, a recrystallization from petroleum ether or acetone was carried out. Details of the microanalyses[52] (C, H, N, Cl, and, in one instance, Br) and of the infrared (KBr) and PMR (CD_3CN) spectra are recorded elsewhere.[2]

In a typical procedure, 50 mL of a benzene solution 0.0401 M in methyl perchlorate and 0.12 M in *N,N*-dimethylaniline was allowed to react at room temperature for 2 weeks. After filtration, the precipitate was washed twice with benzene and dried under vacuum to give 0.462 g (98%) of a white solid, identified as *N,N,N*-trimethylanilinium perchlorate: mp 178-179 °C; IR (KBr) includes 8-10 μ (broad); NMR (CD_3CN) δ 3.54 (s, 9 H), 7.45-7.87 (m, 5 H). Anal. Calcd for $C_9H_{14}NClO_4$: C, 45.82; H, 5.98; N, 5.94; Cl, 15.04. Found: C, 45.65; H, 5.92; N, 5.90; Cl, 14.91.

The percentage yields and melting points (°C) of other isolated products were as follows.

(a) For varying X in $(XC_6H_4NMe_3)^+ClO_4^-$: *p*-OMe, 98, 190.5-191; *p*-Me, 99, 194.5-195.5; *m*-Me, 97, 136-137; *p*-Br, 97, 250 dec; *m*-Cl, 91, 157.5-160; *p*-CN, 93, 162-163.5; *m*-NO_2, 97, 208 dec; *p*-NO_2, 92, 175.5-177.

(b) For varying X in $(XC_6H_4NMe_2Et)^+ClO_4^-$: *p*-Me, 99, 64-66.5; *m*-Me, 97, 103-104.5; H, 97, 90-91; *m*-Cl, 92, 93.2-94.

(c) For varying X in $(XC_6H_4NMe_2\text{-}i\text{-}Pr)^+ClO_4^-$: *m*-Me, 80, 106.5-107.3; *m*-Cl, 60, 103.8-105.

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[52] Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

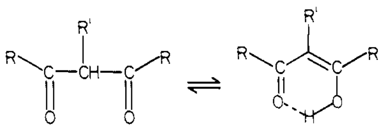
Structural Aspects and Low-Temperature Photochemistry of the Monothioacetylacetone System

Jerzy Gebicki[1] and Allen Krantz*

Contribution from the Departments of Chemistry and Pharmacological Sciences, State University of New York, Stony Brook, New York 11794. *Received October 16, 1980*

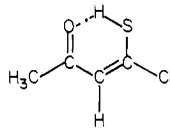
Abstract: New spectroscopic evidence, which is obtained from low-temperature studies of matrix-isolated monothioacetylacetone (TAA), forces a reformulation of the composition and photochemistry of the system. The infrared spectrum of matrix-isolated TAA, which consists primarily of two substances, A and B, clearly indicates the predominant species (A) to be the chelated thioenol (*Z*)-4-mercaptopent-3-en-2-one (**4**). The minor component B, whose concentration can be substantially increased at cryogenic temperatures by irradiation of TAA with light (λ ~350 nm), exhibits nonchelated S-H, C=C, and C=O stretches in the IR, which correlate with a $\lambda_{max}{}^{Ar}$ 279-nm band in the UV spectrum of the system. These spectral data and the fact that B thermally reverts to **4** at ~130 K are uniquely compatible with the assignment of the conformer of **4**, (2-*s*-*trans*)-(*Z*)-4-mercaptopent-3-en-2-one (**5**), to the minor component. Primary photochemical events in the acetylacetone system (AA) appear to parallel those occurring in TAA.

β-Diketones **1** are known to exist in equilibrium with the corresponding chelated enolic tautomers, **2**. The composition of the system is dependent upon both the pattern of substitution on the carbon framework, and the external environment.[2] For simple alkyl substituents (R = alkyl, R′ = H) the *Z*-chelate **2** is favored in the gas phase and in nonpolar or hydrocarbon solvents. When R′ = alkyl or aralkyl, the proportion of enol is reduced substantially, presumably owing to unfavorable steric interactions.

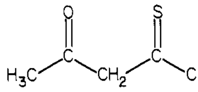


1 2

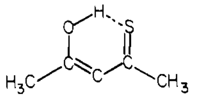
As an analogue of the enolizable β-diketones, the monothioacetylacetone system (TAA)[3] is of interest, particularly with respect to the influence of the sulfur atom on kinetic and thermodynamic relations amongst the various rotamers and tautomers that occupy energy minima. However, reports detailing the composition of TAA have been contradictory.[4-10] There is no general agreement as to what extent TAA distributes amongst each chelated *Z*-tautomer **4** and **9**, their conformers or geometrical isomers, or the monothioacetylacetone tautomer, **3**.



4



3



9

A current view, promoted by Duus and co-workers,[9,10] is that TAA consists of two chelated forms, **9** and **4**, at room temperature, with the enol dominating by perhaps a factor of 2 or 3.

The argument for the enol **9**–enethiol **4** equilibrium as characterizing the TAA system, with **9** dominating, rests on (a) the

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[1] On leave from the Institute of Applied Radiation Chemistry, Technical University, Lódź, Poland.

[2] Forsen, S.; Nilsson, M. In "The Chemistry of the Carbonyl Group"; Zabicky, J., Ed.; Interscience: New York, 1970.

[3] TAA refers to those species that comprise the monothioacetylacetone *system* and not necessarily **3** itself.

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