Kurze Mitteilungen

Bis am 15. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht. Es werden auch Manuskripte aus dem Ausland angenommen

The Bromometric Determination of Enol Contents of Benzoylacetanilide and Acetoacetanilide*

Summary

The enolization of acetoacetanilide (AAA) and benzoylacetanilide (BAA) has been studied in ethanol, methanol, dioxane and their water mixtures, by a bromometric method. The dependance of the amount of bound bromine upon the time interval between addition of bromine and quenching with phenol has been determined. The largest influence on the results was noted in polar solvents. On the assumption that bromination occurs instantaneously, discrete quench time results were extrapolated to zero time and enol contents at zero quench time have been calculated.

Introduction

The determination of the enol content of β-diketones and β-ketoesters is of great importance in many physicochemical investigations. The most commonly used technique is that of MEYER[1-2] which is based upon the bromination of the enol «double bond». The possibility of a rapid keto-enol tautomerism during the analysis has not been considered. Several investigators[3-6] tried to limit this possibility. IR and ultraviolet techniques have also been employed[5,6] to find the enol percentage but the results were only semi-quantitative. The most important spectral techniques at present is high resolution proton NMR but it has limited application because many solvents are protonic themselves and interfere with the measurement of the tautomer resonance[7-9]. Recently MANKAD *et al.*[10] have studied the enol contents in acetoacetarylamides by MEYER's technique.

The present studies were undertaken to obtain the total enol contents of benzoylacetanilide (BAA) and acetoacetanilide (AAA) in various solvent—water mixtures by using the bromometric method[11]. Attempt has been made to determine the dependance of enol contents on the time interval between the addition of bromine and quenching with phenol in solvents using the method suggested by LOCHMULLER[12].

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Experimental

Reagents: The compounds AAA and BAA used were obtained from Aldrich Chemicals Co. Inc., Milwaukee (U.S.A.). All solvents and chemicals used were of Analar grade.

Bromometric Measurements:

An established[11], indirect bromometric procedure was used for all measurements. The technique involves the addition of excess of bromine to 0.1 M solution of AAA and 0.02 M solution of BAA resp. in different solvent–water mixtures. The excess of bromine was quenched at a fixed time interval with an excess of phenol. Bromoketone thus formed was treated with excess of KI solution and the liberated iodine was titrated with standard sodium thiosulphate solution. In order to establish the effect of quench time on the observed results, three replicate determinations were made at an average of four different equispaced quench time intervals. The standard deviation of the mean ranged from 1 to 2% enol.

All measurements were made at 35 ± 1 °C. The samples were equilibrated for 24 to 30 hours at the experimental temperature before analysis. A blank consisting of the solvent alone was run at each quenching time.

Determination of enol % at zero quench time:

The enol content at zero quench time was obtained by the extrapolation of the data obtained at various quench times to zero seconds. The extrapolation was accomplished by polynomial least square regression analysis. This computation was accomplished by a programme POLRG from the Scientific Subroutine Package (SSP) for the IBM 1130 computing system. The data were fitted to a function of the general form

$$t = \text{time (sec)};\ t_0 = \text{enol \% at } t = 0 \text{ sec},$$
$$\text{Enol \%} = t_0 + a_1 t_1 + a_2 t_2^2 + a_3 t_3^3 + \cdots .$$

Several polynomial orders were tried for each sample and the results reported are those derived from the fit which gave the smallest residual sum of squares. The indeterminancy in the value of «t_0» averaged 2 to 3% relative.

Results and Discussion

The results of the bromometric determinations are shown in Table 1. The strong dependance of the observed enol contents on the time interval between the addition of bromine and the quenching agent, phenol, is quite evident from Table 1 and 2. The effect (Fig. 1) is quite dramatic in the polar solvents (e.g. 16.6% methanol by weight) where a difference of forty seconds results in a relative increase of over 100% enol contents. If the bromination process is assumed to be instantaneous over the time period of the experiment, then it is possible to extrapolate to zero second quench time from the data obtained at fixed quench times. This was done and re-

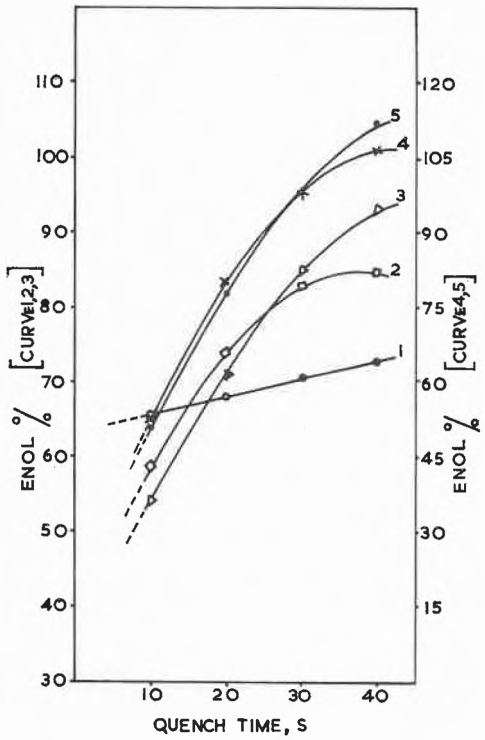
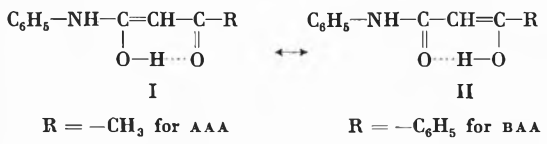


Fig. 1. Enol % at various quench times for AAA at 35 °C in methanol and methanol—water mixture (methanol % by weight)

Curve 1: in methanol
Curve 2: 76.2% methanol
Curve 3: 54.6% methanol
Curve 4: 34.7% methanol
Curve 5: 16.6% methanol

sults are reported in Table 1 and 2 under the heading «t_0».

It can be seen that the percentage of enol in AAA and BAA is less in the solvents of high polarity and vice versa. Since the keto form of a diketone is almost invariably more polar than the enol form, the enol/keto ratio for a given pair of tautomers at equilibrium in solution depends markedly on the polarity of the solvent and that this ratio tends to be greatest in the least polar solvents[13]. As is also generally known a solvent with a high dielectric constant destroys the internal hydrogen bonding (Structure I and II)



I II

R = $-CH_3$ for AAA R = $-C_6H_5$ for BAA

The importance of the internal hydrogen bonding is indicated by the decrease in enolization of AAA to 13.27% in 16.40% (by weight) ethanol where the carbonyl group can be hydrogen bonded to water molecules[14]. The analysis of the results in the cases of more polar solvents, were the values are in excess of 100% enol at longer quenching time, suggests a second enolization process involving the bromoketone formed in the first instance. Hence the technique of extrapolation to zero quench time can yield results which are generally valid.

Table 1. Observed Enol % at Various Quench Times for Acetoacetanilide at 35 °C in Various Solvent Mixtures

Weight % Organic Solvent	Time (sec) 10	20	30	40	t_0
Ethanol—Water					
100.0	72.63	77.53	79.55	80.70	66.36
75.8	54.08	68.01	80.33	89.35	37.27
54.0	52.28	72.08	91.94	105.20	27.55
16.4	46.22	76.36	98.40	106.06	13.27
Methanol—Water					
100.0	66.03	68.24	70.70	72.91	63.69
76.2	58.80	74.06	82.97	84.69	36.56
54.6	54.00	71.02	84.94	93.28	32.02
34.7	53.50	80.27	98.00	106.14	17.23
16.6	50.47	78.00	98.00	112.00	16.56
Dioxane—Water					
100.0	85.89	90.21	93.38	97.96	82.34
80.5	46.03	53.32	58.22	64.02	38.82
60.8	39.15	48.13	54.76	60.81	29.12
40.8	40.89	49.74	59.64	63.41	27.67
20.5	31.13	43.23	53.70	62.83	17.62

Table 2. Observed Enol % at Various Quench Times for Benzoylacetanilide at 35 °C in Various Solvent Mixtures

Weight % Organic Solvent	Time (sec) 10	20	30	40	t_0
Ethanol—Water					
100.0	71.17	72.51	75.20	77.90	70.17
75.8	60.43	75.80	85.94	89.97	39.17
54.0	59.08	77.50	87.30	96.68	38.19
Methanol—Water					
100.0	66.09	68.53	70.98	73.43	63.64
76.2	47.73	59.97	67.06	79.55	38.20
54.6	48.95	62.41	72.20	78.32	31.82
Dioxane—Water					
100.00	78.20	79.80	83.40	86.10	76.43
80.50	68.97	76.15	79.03	81.90	60.71
60.80	60.35	74.72	83.34	93.40	45.62
45.80	54.60	67.53	96.27	114.95	38.08

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Einstufige Herstellung von Nitrilen aus Carbonsäuren

Summary

The formation of nitriles from carboxylic acids by a one step process, using urea and aminosulfonic acid is described.

Es ist bekannt, Nitrile herzustellen, indem man ein Gemisch aus einer Carbonsäure oder einem ihrer Säurederivate und Harnstoff auf eine Temperatur über 250° erhitzt[1]. Ebenso ist die Herstellung von Sebacinsäuredinitril und Cyanpelargonsäure aus Sebacinsäure mittels Harnstoff bei 160 bis 220° bekannt[2].

Die erstgenannte Reaktion verläuft bei gewissen Carbonsäuren oder deren Säurederivaten rascher und bei niedrigeren Temperaturen, wenn dem Reaktionsgemisch Amidosulfosäure zugegeben wird[3].

So geht z.B. *o*-Chlorbenzoesäure (1 Mol) bei einstündigem Erhitzen mit Amidosulfosäure (1,5 bis 2 Mol) und Harnstoff (1 bis 1,5 Mol) auf 200 bis 240° in *o*-Chlorbenzonitril über, das in einer Ausbeute von etwa 85 bis 90% der Theorie anfällt. Unter denselben Bedingungen entstehen bei Abwesenheit von Amidosulfosäure etwa 50% Amid, bei Abwesenheit von Harnstoff nur etwa 7% Nitril.

Die Aufarbeitung des hergestellten Nitrils erfolgt entweder durch Ausgießen auf Wasser, Filtrieren und Waschen (I), durch Destillation (II) oder durch Extraktion mit organischen Lösungsmitteln, wie z.B. Chloroform, Trichloräthylen, Perchloräthylen, Cyclohexan oder Benzol und Einengen dieser Lösungen zur Kristallisation der Nitrile (III).

Zur Veranschaulichung der Leistungsfähigkeit des oben am Beispiel des *o*-Chlorbenzonitrils beschriebenen Verfahrens stellen wir tabellarisch die Ausbeuten einer Auswahl aus den entsprechenden Carbonsäuren hergestellter Nitrile zusammen (Tabelle 1).

Tabelle 1

Nitril	Ausbeute % der Theorie	Aufarbeitung
Phenylaceto-	48%	II
Cyclohexancarbonsäure-	69%	III + II
Thiophen-2-carbonsäure	30%	III + II
Nicotinsäure	80%	III
Benzo-	75%	III + II
	51% [b]	
4-Methyl-benzo-	57%	III
2-Fluor-benzo-	75%	II
2-Chlor-benzo-	87%	II oder I
	*68% [b]	II oder I
	*82% [c]	
	*82% [d]	
	*82% [e]	
3-Chlor-benzo-	62%	III
4-Chlor-benzo-	56%	III
2-Brom-benzo-	86%	III
2-Jod-benzo-	90%	III
2-Nitro-benzo-	51%	III
3-Nitro-benzo-	46%	III
4-Nitro-benzo-	72%	III
2-Chlor-5-nitro-benzo-	66%	III
Naphthalin-1-1-carbonsäure	48%	III

* Ausgangsprodukt: b) Trihalogenmethylderivat
c) Carbonsäureanhydrid
d) Ammoniumsalz der Carbonsäure
e) Natriumsalz der Carbonsäure

Alle Nitrile wurden durch Schmelzpunkt- (bzw. Siedepunkt)-, Elementaranalyse und NMR-Spektrum identifiziert.

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