ISOCYANATE CLEAVAGE OF AMIDES OF 3-OXOACIDS

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N-Substituted amides of α,α-disubstituted 3-oxoacids split at temperatures around 200°C, virtually in a quantitative manner, to form isocyanate and ketone, so that the reaction can be used for preparation purposes. The rate of cleavage of N-alkylamides of 2,2,4-trimethyl-3-oxovaleric acid at 250°C increases with the increasing bulk of the substituent on the nitrogen atom. The effect of the substituents on the nitrogen atom upon the thermolysis in the melt can be explained as a combination of polar, steric, and association effects. It seems that the latter ones, and particularly the hydrophobic interactions, are of a special importance in the evaluation of this effect. It followed from the kinetic study of some N-substituted amides of 2,2,4-trimethyl-3-oxovaleric acid that the isocyanate cleavage occurred by a monomolecular cyclic elimination mechanism.

N-Substituted amides of β-keto acids are unstable at elevated temperatures. Thus, while heated, acetoacetamides either undergo cyclization by autocondensation[1], or split thermolytically (above 350°C) to yield isocyanate and ketone[2]. The isocyanate cleavage also occurs in the photolysis of acetoacetanilides[3]. Thermolysis of keto amides monosubstituted on the α-carbon atom yields stable uracil cycles, the formation of which can also be explained as a consequence of the isocyanate cleavage[3]. It was established from the investigation of the activation of β-keto amides in the anionic polymerization of caprolactam that the cleavage of the β-keto amide N-anion[4] yields isocyanate.

The isolation of N,N'-diphenylurea has been considered as evidence for the formation of methyl isocyanate during the base catalyzed thermolysis of N-2,2,4-tetramethyl-2-oxopentaneamide in the presence of aniline[5]. From the reaction products formed in the base catalyzed reaction in the absence of aniline, diisopropyl ketone, N-methylisobutyramide and 1,3,5,5-tetramethylbarbituric acid[5] were isolated.

A closer study of the above reaction is important from the viewpoint of the disappearance of the β-keto amide structures in anionic lactam polymers, and in particular from the viewpoint of the use of β-keto amides as activators of the anionic polymerization of caprolactam. Moreover, the reaction could also be used for preparation purposes.

EXPERIMENTAL

Melting points were determined under a microscope with a heated stage (Boetius). Infrared spectra were recorded with a Perkin-Elmer 457 apparatus.

Materials Used

Lactone of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid was prepared according to ref.[6] from 2,2,4,4-tetramethyl-1,3-cyclobutadione; b.p. 120–122°C/150 Torr, n_D^{20} 1·4380.

Amides of 2,2,4-trimethyl-3-oxovaleric acid were prepared by an addition of amines to the above lactone, similarly to ref.[6]. The properties and analytical values are summarized in Table I. 2-Benzoyl-2-ethylacetanilide was prepared by ethylation of benzoylacetanilide similarly to ref.[9]. 2-Benzoyl-2-methyl-butyranilide was obtained by methylation of the preceding product, similar to alkylations of benzoylacetanilides; yield 65%, m.p. 107–108°C (ethanol); according to ref.[9], m.p. 107·5–108·2°C.

N,N-*Diethylamide of* p-*toluenesulfonic acid.* From *p*-toluenesulfochloride and diethyl amine; m.p. = 61–62°C (n-heptane); lit.[10], m.p. 63°C.

N-Substituted N'-phenylureas were prepared by a reaction of phenyl isocyanate with individual amines (in a 10% excess) in n-heptane. On mixing the cooled solutions they were left to stand overnight; the precipitated crystalline products were filtered and recrystallized from ethanol or n-heptane. These compounds were then used as reference compounds (*cf.* Table II).

Paraffin oil. Commercial product, quality as required by IR, was distilled twice with lithium aluminium hydride at 2–3 Torr through a short column (Berl saddles); after the third distillation (without addition of lithium aluminium hydride) the fraction boiling at 195–215°C/2–2·5 Torr was collected.

Thermolysis

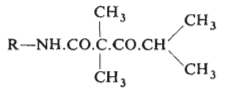
All thermolytic experiments were carried out in a constant flow (18–30 ml/min) of argon purified from oxygen on a Cu-catalyst and dried on a molecular sieve (type 5A). The temperature of the baths was maintained within the range of ±0·2°C.

Identification of products: Keto amide (c. 1 g) was weighed into a thermolytic apparatus (Fig. 1) and heated to 250°C. After a sufficient quantity of the product had been distilled, aniline was added to one part of the distillate diluted with n-heptane, and the solution was left to stand overnight. The product thus obtained was filtered and recrystallized. Infrared spectra (KBr pellets) were identical with those of the authentic N-substituted N'-phenylureas. The mixed melting points also showed no depression (*cf.* Table II). From a further fraction of the distillate, 2,4-dinitrophenylhydrazone of diisopropyl ketone was prepared. The crude hydrazone was purified by chromatography (silicagel, benzene) and recrystallized from n-heptane; m.p. 93·1–94·5°C, 91–92°C, ref.[18]. The infrared spectrum was identical with that of the authentic compounds. The infrared spectrum of one part of the distillate was also measured (capillary – between KBr plates). For all the investigated keto amides, an intense absorption band near 2280 cm^{-1} was observed, corresponding to the group —N=C=O (ref.[19]) (in the case of N,N-dimethylhydrazide the absorption band was situated near 2340 cm^{-1}).

Isocyanate and diisopropyl ketone were determined quantitatively by infrared spectroscopy in tetrachloromethane, using molar extinction coefficients determined at 1715 cm^{-1} for diisopropyl ketone (ε = 320; ref.[20] gives for aliphatic saturated ketones ε = 180–190) and at 2280 cm^{-1} for phenyl isocyanate (ε = 1540, ref.[21] gives ε = 1500) and n-butyl isocyanate (ε = 920).

TABLE I

N-Substituted Amides of 2,2,4-Trimethyl-3-oxovaleric Acid



R	Composition (m.w.)	Calculated/Found			M.p. °C
		% C	% H	% N	
CH_3	$C_9H_{17}NO_2$	63·13	10·00	8·18	52 — 53[a]
	(171·2)	63·12	10·04	8·35	
C_2H_5	$C_{10}H_{19}NO_2$	64·83	10·34	7·56	51 — 52[b]
	(185·1)	64·05	10·31	7·51	
n-C_3H_7	$C_{11}H_{21}NO_2$	66·29	10·62	7·03	36 — 37·5
	(199·3)	66·00	10·62	6·92	
n-C_4H_9	$C_{12}H_{23}NO_2$	67·61	10·87	6·57	34 — 35[c]
	(213·3)	67·72	11·06	6·46	
i-C_4H_9	$C_{12}H_{23}NO_2$	67·61	10·87	6·57	39 — 40
	(213·3)	67·53	10·89	6·80	
s-C_4H_9	$C_{12}H_{23}NO_2$	67·61	10·87	6·57	47·5— 48·5
	(213·3)	67·68	11·10	6·72	
t-C_4H_9	$C_{12}H_{23}NO_2$	67·61	10·87	6·57	81·5— 82[d]
	(213·3)	67·59	10·86	6·52	
C_6H_{11}	$C_{14}H_{25}NO_2$	70·25	10·53	5·85	92— 92·5[e]
(cyclo)	(239·4)	70·53	10·61	5·81	
$C_6H_5.OH_2$	$C_{15}H_{21}NO_2$	72·84	8·56	5·66	71·5— 74·5
	(247·3)	73·24	8·85	5·48	
$(CH_3)_2N$	$C_{10}H_{20}N_2O_2$	59·97	10·07	13·99	74·5— 75·5
	(200·3)	60·19	10·15	13·94	
C_6H_5	$C_{14}H_{19}NO_2$	77·07	8·21	6·00	94 — 94·5[f]
	(233·3)	72·21	8·42	5·87	
p-$CH_3.C_6H_4$	$C_{15}H_{21}NO_2$	72·90	8·50	5·91	85·5— 86
	(247·3)	73·08	8·71	5·83	
m-$CH_3.C_6H_4$	$C_{15}H_{21}NO_2$	72·90	8·50	5·91	86 — 87
	(247·3)	73·11	8·62	5·79	
p-$CH_3O.C_6H_4$	$C_{15}H_{21}NO_3$	68·50	8·04	5·32	95 — 96
	(263·3)	68·72	8·30	5·56	
m-$CH_3O.C_6H_4$	$C_{15}H_{21}NO_3$	68·50	8·04	5·32	100·5— 102·5
	(263·3)	68·41	8·08	5·15	
p-$(C_2H_5)_2N.C_6H_4$	$C_{18}H_{28}N_2O_2$	71·10	9·20	9·20	111— 112
	(304·4)	71·29	9·11	9·35	

[a] M.p. 55°C, ref.[5]; [b] M.p. 50—51°C, ref.[6]; [c] M.p. 30—31°C, ref.[7]; [d] M.p. 81—82°C, ref.[8]; [e] M.p. 92—96°C (ethanol–water), ref.[7]; [f] M.p. 94—95°C, ref.[6].

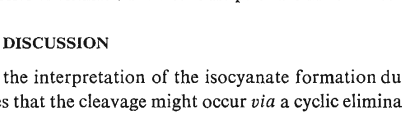
In the case of the other isocyanates, extinction coefficients used were determined indirectly from the ratio of extinctions of diisopropyl ketone and the individual isocyanates. The amount of keto amide in the distillate was determined from the extinction in the region around 1 680 cm^{-1}; for anilide ($\varepsilon = 870$), ethyl amide ($\varepsilon = 641$), propyl amide ($\varepsilon = 668$), n-butyl amide ($\varepsilon = 740$), t-butyl amide ($\varepsilon = 750$), and benzyl amide ($\varepsilon = 651$). In some cases the extent of the reaction was determined from the amount of the distillate and the weight loss of keto amide (Table III). The determination by infrared spectroscopy was verified by gas chromatography (when the quantitative character of cleavage had to be verified) (*cf.* Table IV).

Thermolysis in a closed system: Butyl isocyanate, n-butylamide of 2,2,4-trimethyl-3-oxovaleric acid, or a mixture thereof were weighed into ampoules, 10 ml in volume (well dried, with air replaced by argon). The sealed ampoules were thermostated to 250°C for 24 h, cooled, the contents were transferred into tetrachloromethane, and the extinctions of isocyanate, ketone and keto amide were measured. The results are listed in Table V.

Thermolysis in an open system: Keto amide, or a solvent and keto amide were weighed into the apparatus (Fig. 1); the keto amide or its solution was thermolysed in a flow of inert gas. At the same time, one part of the apparatus was heated to the temperature of the vapours of the distillate. The distillate was collected in a freezing trap separated from the air atmosphere by a paraffin oil trap. The distillate was then treated, either for purposes of identification or quantitative determination. In the course of thermolysis, distillates were collected in certain time intervals by changing the freezing traps; then the distillate was transferred quantitatively into tetrachloromethane, and the absorption was measured in the region of the analytical band of isocyanate, ketone and amide carbonyl. The exchange of the freezing traps took 5—10 s., which virtually did not lead to any losses of distillate. The results are presented in Table VI.

RESULTS AND DISCUSSION

It was assumed in the interpretation of the isocyanate formation during the pyrolysis of acetoacetanilides that the cleavage might occur *via* a cyclic elimination mechanism[2], similarly to the pyrolysis of ester[22], amine oxides[23], xanthates, *etc.*[24]:



Owing to the presence of a free methylene group in the α-position a large enolization can be expected to take place in acetoacetamides. Since the enol form cannot split to form isocyanate and ketone by the above mechanism, the extent of the isocyanate cleavage in the case of β-keto amides having at least one hydrogen atom on the α-carbon atom will be reduced by competitive enolization. Moreover, β-keto amides having acidic hydrogen atoms on the α-carbon atom undergo a series of side and consecutive reactions (*e.g.*, ref.[1,25]), which also reduce the extent of the isocyanate cleavage.

The α,α-disubstituted keto amides do not enolize, so that the possibility of the occurrence of side and consecutive reactions is greatly reduced. In this work, amides of 2,2,4-trimethyl-3-oxovaleric acid were chosen, which are readily accessible in

TABLE II

Phenylureas R—NH.CO.NH.C_6H_5

R	M.p., °C		R	M.p., °C	
	found	ref.		found	ref.
CH_3	150—152	152—153 (11)	t-C_4H_9	165—166	167—168 (15)
C_2H_5	96— 97·5	98 (12)	Cyclohexyl	179—180	182 (16)
n-C_3H_7	113—114·5	114—116 (13)	Phenyl	221—223·5	234 (12)
n-C_4H_9	127—128	129—130 (14)	Benzyl	169—170	168—170 (17)

TABLE III

Thermolysis of Keto Amides $(CH_3)_2CH.CO.C(CH_3)_2.CONH$-R at 247°C/5 h

R	Keto amide g	Distillate g	% w/w	Conversion, mol %[a]	
				ketone	isocyanate
Ethyl	1·2668	0·2821	22·3	—	—
n-Propyl	0·9851	0·2561	26·0	27·0	25·3
n-Butyl	1·3231	0·4102	31·0	36·8	35·2
t-Butyl	0·9885	0·8797	89·0	91·0	88·–
Diethylamino	0·9963	0·2462	24·7	22·8	—
Benzyl	1·0170	0·1271	12·5	13·5	—
Cyclohexyl	0·9922	0·4376	44·1	46·7	—

[a] Infrared spectroscopy data.

TABLE IV

Thermolysis of N-n-Butyl-2,2,4-trimethyl-3-oxovaleramide at 267°C and 150 min in an Open System

Keto amide g	Distillate			Distillation residue keto amide
	weight, %	—N=C=O[a]	C=O[a]	
2·0344	0·9365	46·3	45·2	54·9
	46·1	44·9[b]	48·2[b]	
0·9221	0·4290	48·0	46·8	53·8
	47·5			

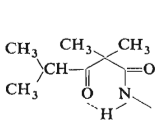
[a] Mol. % referred to the initial ketoamide; [b] by gas chromatographic method.

a high yield and purity from the lactone form of dimeric dimethyl ketene and the corresponding amine (Table I).

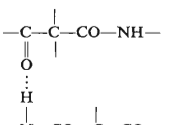
Diisopropyl ketone and the corresponding isocyanates (Table II) were identified in the products of thermolysis of several 2,2,4-trimethyl-3-oxovaleramides. If the forming isocyanates are removed immediately from the thermolyzed keto amide, the reaction is virtually quantitative, so that an investigation of the isocyanate cleavage of keto amides is not complicated with competitive reactions (Table IV). On the contrary, the isocyanate cleavage of keto amides in a closed system can lead to carbamoylation and other side reactions.

Similarly, the thermolysis of N,2,2,4-tetramethyl-2-oxopentaneamide in the presence of bases[5] has been found to proceed in a complicated manner. When heating an equimolar mixture of n-butyl isocyanate and N-n-butyl-2,2,4-trimethyl-3-oxovaleramide in a closed system a reaction between keto amide and isocyanate was observed (Table V). This is why an open system was chosen for kinetic measurements of the isocyanate cleavage (Fig. 1).

It was established (Fig. 2) that in solvents of very different dielectric constants, the isocyanate cleavage was of the first order with respect to keto amide. It can be assumed, therefore, that the reaction is of the first order also in the absence of solvents, and can be regarded as an intramolecular rearrangement involving proton migration. The most probable structure of keto amide in the transition state is a cyclic one (*A*), but an intermolecular rearrangement (*B*) can also be considered.



(*A*)



(*B*)

In a strong polar solvent (N,N-diethyl-*p*-toluenesulfonamide), the reaction proceeds slower than in a non-polar hydrocarbon solvent (Fig. 2). The retarding effect of the sulfonamide can be explained by an interference of the hydrogen bond formation between the -NH-group of keto amide with the sulfonamide group of the solvent. The interference with the intramolecular and intermolecular hydrogen bonds of keto amides is much weaker in non-polar solvents and, therefore, the reaction occurs at a higher rate. It can be assumed, moreover, that under the given conditions the participation of the keto amide anions in the formation of isocyanates can be neglected.

It follows from an investigation of the kinetics of the isocyanate cleavage (Tables III and VI) that the kinetic parameters considerably depend on the nature of the sub-

stituents on the nitrogen atom. At 247°C, the rate of cleavage increases in the following order of substituents (Table III and VI): benzyl < ethyl < diethylamino < n-propyl < iso-butyl < n-butyl < cyclohexyl < sec-butyl < *m*-methoxyphenyl < phenyl < tert-butyl < *p*-tolyl < *m*-tolyl. The above order, however, is valid only for the given temperature and can differ owing to different activation energies (Table VI) at different temperatures. The effect of substituents on the nitrogen atom cannot be correlated with the induction effect by applying the Hammet or Taft correlation. The effect of substituents on the isocyanate cleavage can rather be explained in terms of steric or association effects influencing the formation of either intra- or intermolecular hydrogen bonds.

It can be expected that the extent of association, and consequently the degree of ordering of the reacting system will be affected by the nature of the solvent. For the thermolysis of N-butyl keto amide the highest activation entropy was found in N,N-diethyl-*p*-toluenesulfonamide; in the case of thermolysis without solvent the value of S^* was lower, and that in a hydrocarbon was the lowest (Table VI). The highest solvation of ketoamide with solvent can be expected in the system ketoamide–polar solvent, so that such a system will be much more ordered than that with a non-polar solvent. The formation of the cyclic transition state leads to a lower degree of ordering of the whole system in the case of a polar solvent, since the solvent can associate with the hydrogen atom of the amide group (which has already associated intramolecularly with the keto carbonyl) to a lower extent than in the initial state. Accord-

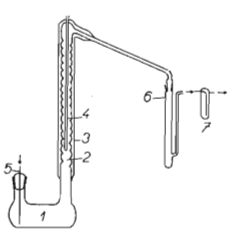


FIG. 1

Apparatus for Thermolysis

1 Reactor; *2* column; *3* heating jacket; *4* thermocouple pocket; *5* tube for the inert gas (capillary); *6* freezing trap; *7* bubbler with paraffin oil.

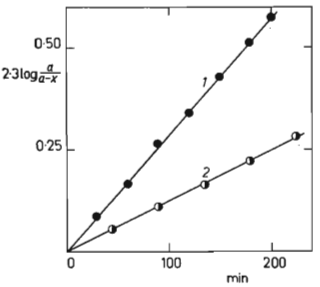


FIG. 2

Thermolysis of N-n-Butyl-2,2,4-trimethyl-3-oxovaleramide in Paraffin Oil ($4{\cdot}4 \cdot 10^{-4}$ mol/g) at 248·8°C *1* and in N,N-diethyl-*p*-toluenesulfonamide ($4{\cdot}7 \times 10^{-4}$ mol/g) at 247°C *2*.

ingly, the activation entropy in N,N-diethyl-*p*-toluenesulfonamide has a high positive value (20·5 e.u.) compared with a small negative value (−1·6 e.u.) of the activation entropy in the thermolysis carried out in paraffin oil. The activation energy varies accordingly, being lower in the case of thermolysis carried out in paraffin oil (39·4) than of that in polar diethyl-*p*-toluenesulfonamide (49·7). The thermolysis of keto amide in the absence of solvent can be regarded upon similarly as that in a solvent,

TABLE V

Thermolysis of N-n-Butyl-2,2,4-trimethyl-3-oxovaleramide (B), Butyl Isocyanate (A) and a Mixture thereof in a Closed System at 247°C for 24 h

Designation	Weighed amount g	Extinction −N=C=O	
		Calculated	Found
A	0·0655	0·610	0·600
B	0·1205	0·520	0·326
C	0·1206 B 0·0476 A	0·907	0·532

TABLE VI

Kinetic Parameters of the Thermolysis of Keto Amides $(CH_3)_2CH.CO.C(CH_3)_2.CO.NH\text{-}R$ in the Melt

R	E_a kcal mol^{-1}	A min^{-1}	$S^{\ddagger}_{510}$ e. u.
Ethyl	18·78	$6{\cdot}02 \cdot 10^{4}$	−39·80
n-Propyl	35·80	$1{\cdot}10^{12}$	− 6·5
n-Butyl	44·00	$4{\cdot}42 \cdot 10^{15}$	9·90
n-Butyl[a]	39·40	$1{\cdot}21 \cdot 10^{13}$	− 1·57
n-Butyl[b]	49·70	$9{\cdot}00 \cdot 10^{17}$	20·53
i-Butyl	39·20	$3{\cdot}55 \cdot 10^{13}$	0·40
sec-Butyl	31·55	$5{\cdot}31 \cdot 10^{10}$	−12·60
tert-Butyl	20·40	$4{\cdot}04 \cdot 10^{6}$	−33·90
Phenyl	39·80	$3{\cdot}31 \cdot 10^{14}$	5·00
p-Methylphenyl	48·10	$1{\cdot}11 \cdot 10^{18}$	29·70
m-Methylphenyl	44·60	$4{\cdot}64 \cdot 10^{16}$	14·50
m-Methoxyphenyl	37·80	$4{\cdot}60 \cdot 10^{13}$	0·80

[a] In paraffin oil at $c_0 = 5 \cdot 10^{-4}$ mol/g; [b] in N,N-diethyl-*p*-toluenesulfonamide at $c_0 = 5 \cdot 10^{-4}$ mol/g.

which in this case is represented by keto amide. As can be seen in Table VI, the activation entropy without solvent has a lower positive value than that in N,N-diethyl-*p*-toluenesulfonamide. This can be explained by a lower solvation ability of the amide carbonyl group as compared with a higher solvation ability of the sulfonyl group. When estimating the effects of various substituents on the nitrogen atom of keto amide upon thermolysis in the melt the above autosolvation cannot be omitted.

The effect of the increasing length of substituents could be similar to that due to diluting with a hydrocarbon. With increasing concentration of the diluent an increase in the difference between the ordering in the transition and initial states should be expected, since cyclization is favourized by dilution. For these reasons, entropy should decrease with increasing dilution. What is observed in the series of the investigated alkyl substituents, however, is quite the opposite. In the series of keto amides with unbranched N-alkyl substituents the activation entropy increases with increasing length of the substituent (Table VI). When taking into account that the hydrophobic interaction[26] of substituents on the nitrogen atom also participates in the ordering of the reacting system, then the difference in ordering of both the initial and transition states decreases in the series of substituents with an increasing number of methylene groups (Table VI). A similar situation is found in the series of branched butyl substituents (*cf.* Table VI). The difference in the ordering of the initial and transition states decreases, and the activation entropy increases in the series of isomeric butyl substituents as follows:

$$\text{tert} < \text{sec} < \text{iso} < \text{n}$$

Moreover, steric effects upon the extent of associations, and thus upon the activation entropy, should also be expected with the branched substituents. Thus, *e.g.*, in the tert-butyl group, a conformer becomes important in which the two methyl groups of the substituent enter into a strong intramolecular interaction with the amide carbonyl group, which in its turn lowers the free rotation of the substituent and affects the other interactions. The hydrophobic interaction will be least important in the case of the tert-butyl substituent, similarly to what is observed in the case of a methyl substituent with the lowest activation entropy. A dependence similar to the activation entropy is also found with the activation energy, which increases with the increasing hydrophobic interaction of the N-substituents. An interpretation of the effects of the individual substituents is more difficult in the aromatic series, because the extent of hydrophobic interactions of the aryl substituents is also affected by polar effects.

The values of the frequency factors of some keto amides are very low (Table VI), which is unusual for monomolecular reactions[27]. For similar thermolytic reactions, occurring *via* a monomolecular cyclic elimination mechanism, frequency factors around $10^{12}-10^{13}$ were observed[24]. In the melt of keto amide, which at the same

time acts as a solvent, a degradation of the reaction order can occur and the isocyanate cleavage can proceed as a pseudomonomolecular reaction. It cannot be excluded, therefore, that the isocyanate cleavage in the melt can also occur *via* bimolecular mechanism.

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