KINETIC STUDY OF OXIME-FORMING REACTIONS OF KETONES

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Kinetic results confirm the activity sequence to be expected in theory for the reaction rates. For further studies it appears necessary to determine more exactly the overall reaction order and to describe the instantaneous variations in the reaction order by means of a mathematical formula. The UV spectrophotometric procedure applied, requiring only small amounts of material, can be automated and appears advantageous for future studies with respect to the possibility of a relatively fast data processing.

Kinetic measurements were made on the oxime-forming reactions of alicyclic, monocyclic and bicyclic ketones, and the data obtained were compared. Besides earlier titrimetric comparisons, efforts were also made to follow the change in the ultraviolet absorption maximum of hydroxylamine salicylate under the conditions of the reaction. The results as well as the possibility of a more exact approach to the kinetic values are dealt with in the present paper.

Experimental

The oxime-forming reaction was carried out in a 2:1 mixture of methanol—chloroform, under the conditions described by GÖRÖG *et al.* [1]. The volume of the reaction mixture was always 200 ml. The reaction space was thermostated, and samples were taken with a pump-system sampler. The reaction mixture was stirred from the addition of the hydroxylamine salicylate. The reagent was prepared by the procedure described in [1].

The reaction in the samples was stopped by instantaneous cooling to $-20\,^{\circ}C$. The consumption was followed titrimetrically, as described earlier [2]. Titration was performed at $-20\,^{\circ}C$ immediately after the sampling. For sake of comparability, the concentrations of ketones and hydroxylamine salicylate in the reaction mixture were kept constant. Partial orders were determined applying concentrations varied between wide limits [2].

Spectra were recorded with a SPECORD (GDR) spectrophotometer. The spectrophotometric procedure did not serve merely as a check. The accuracy of the method was tested during these measurements and was about $\pm 1\%$ disregarding the possibility of subjective error. The spectrophotometer cell was provided with

a micro-stirrer, and the addition of the reagent was instantaneous here, too. Measurements were made at 25 °C. The error can be decreased by thermostating.

The results were evaluated by means of a calibration curve prepared previously. The spectrogram obtained for 4-*t*-butylcyclohexanone is shown in Fig. 1. In both methods the concentrations of ketones used was in the range 0.0016—0.1500 mole. Studies were made at 20, 25, and 30 °C. For cyclohexanone the reaction could be followed only at 0 °C. Calculations were performed with a MINSK-22 computer.

On the basis of previous studies [2], the overall order of reaction was taken as 2. The rate constants of the reaction were determined using the equation

$$k\tau = \frac{1}{n-1}\left[\frac{1}{([A_0]-[X])^{n-1}} - \frac{1}{A_0^{n-1}}\right],$$

where n=2. Activation enthalpies were calculated from the equation

$$k = Ae^{-\frac{H^{\ddagger}}{RT}}.$$

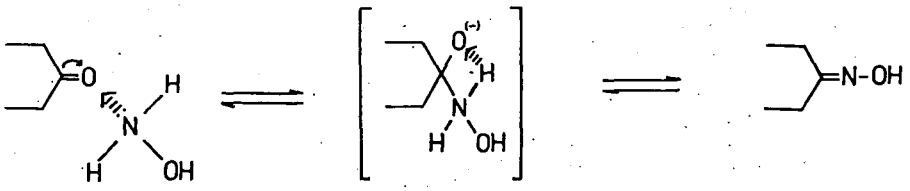
The rate constants were obtained as mean values within the standard deviation.

Results and discussion

Fig. 1. shows the UV spectrum of 4-*t*-butylcyclohexanone. The results are listed in Table I.

The theoretically expected sequence of the reaction rates holds for the monocyclic ketones. This is illustrated in Fig. 2, where the logarithms of the reaction rates are plotted as a function of the ring size for the three temperatures studied.

The reaction steps of oxime-formation are as follows:



Deviations in the *k* values indicate not only the relative errors in the titration method; they also show that the second-order equation is only a good approximation but does not describe exactly the kinetics of the reaction in all cases. Accordingly, it would be desirable to slow down the reaction so that the individual steps could be followed. Since the H^+-dissociation of methanol exerts an influence on the incorporation of the proton, the use of deuterated hydroxylamine in chloroform appears to be suitable for studying the first step.

It can be seen from Table I that the highest reaction rate was observed for cyclohexanone. In this case the kinetic measurement could be performed only at 0 °C. The decreased activity of 4-*t*-butylcylohexanone can be explained by the effect of the *para* substituent. In this case the bulky *t*-butyl group is always equatorial.

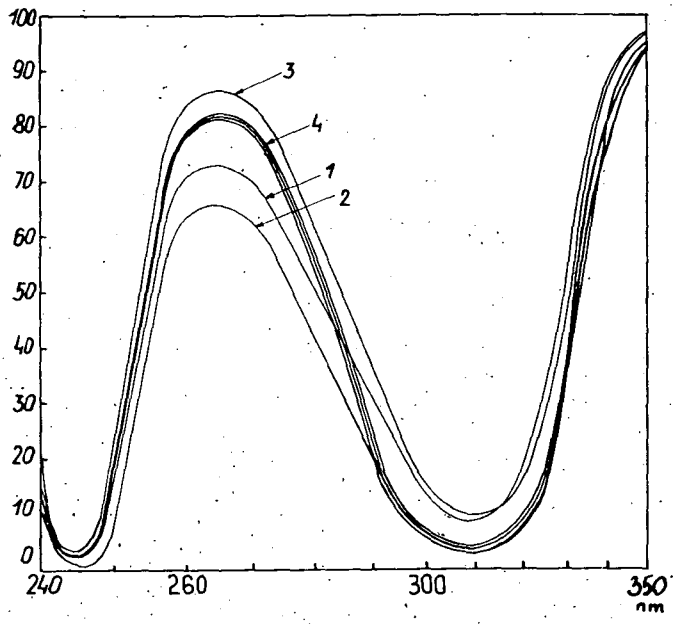


Fig. 1. Curves 1 and 2 are for hydroxylamine salicylate concentrations of $4.0 \cdot 10^{-5}$ mole, and $3.0 \cdot 10^{-5}$ mole, respectively. Curve 3 is the absorption of hydroxylamine salicylate 20 sec after the addition of 4-*t*-butylcyclohexanone to the system. The curves denoted by 4 are the absorptions recorded after 40, 60, etc. sec.

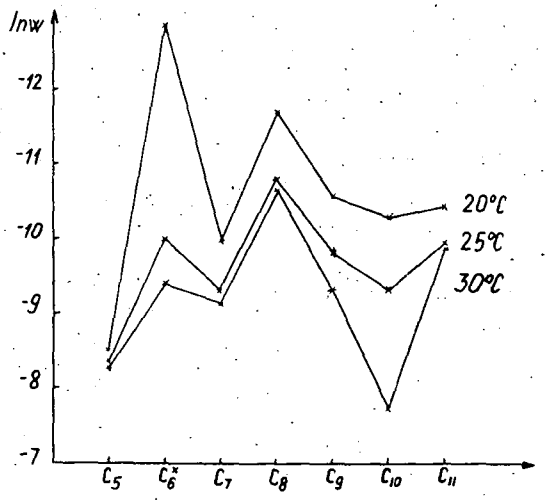


Fig. 2. Logarithmic values of reaction rates plotted as a function of ring size at three different temperatures. $C_6^* = t$-butylcyclohexanone

Table I

Ketone	Concentration mole/l	T °C	ln k	k	lnw	$\Delta H^{\ddagger}$ kcal/mole
Cyclopentenone	0.0499	20	−0.2798	0.7579	−8.5777	2.9286
		25	−0.1212	0.8859	−8.4237	
		30	−0.0711	0.9214	−8.3689	
4-*t*-Butylcyclo-hexanone	0.0050	20	−2.2765	0.1026	−12.8697	0.4576
		25	0.5410	1.7177	−10.0523	
		30	1.1674	3.2137	−9.4258	
Cycloheptanone	0.0040	20	0.6054	1.8319	−9.9934	0.3065
		25	1.2670	3.5502	−9.3317	
		30	1.4211	4.1418	−9.1775	
Cyclooctanone	0.0050	20	−1.0812	0.3392	−11.6798	1.0342
		25	−0.2153	0.8063	−10.8139	
		30	−0.0839	0.9196	−10.6825	
Cyclononanone	0.0050	20	0.0206	1.0208	−10.5775	5.4488
		25	0.7906	2.2048	− 9.8075	
		30	1.9682	7.1576	− 9.3242	
Cyclodecanone	0.0032	20	1.3829	3.9866	−10.3428	6.132
		25	2.4204	11.2501	− 9.3055	
		30	3.3073	27.3123	− 7.7243	
Cyclo-undecanone	0.0029	20	1.3725	3.9452	−10.4574	0.5033
		25	1.5498	4.7106	−10.2801	
		30	1.8973	6.6680	− 9.9326	
α-etralone	0.0050	20	−1.5219	0.2183	−12.1205	3.395
		25	−1.5516	0.2119	−12.0939	
β-etralone	0.0050	20	0.5447	0.5800	−11.1426	0.7408
		25	0.0866	0.9174	−10.6840	
		30	0.4444	1.5596	−10.1534	
Dicyclopropyl-ketone	0.00497	20	−1.3988	0.2469	−12.0044	2.8416
		25	−1.0834	0.3384	−11.6891	
		30	−1.0413	0.3530	−11.6469	
Cyclohexanone	0.0049	0	2.7018	14.9062	− 7.8984	

The rate, decreased for cyclooctanone, increases towards cyclodecanone, and decreases for cycloundecanone again. It is particularly clear from the values measured at 30 °C that the reaction rate of cyclodecanone is higher than that of the following member of the series.

If the activation enthalpies are plotted as a function of the ring size, the resulting curve exhibits a maximum at cyclodecanone, similarly as observed for the combustion heat per methylene group in the alicyclic hydrocarbons.

The reaction rate of α-tetralone is lower than that of β-tetralone, and this appears also in the differences observed in their activation enthalpies. This is due to the

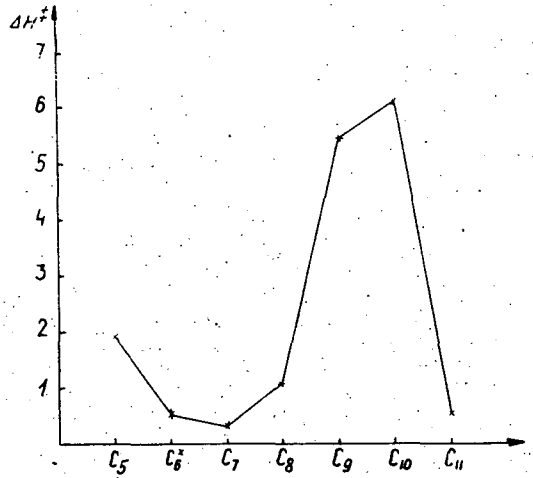


Fig. 3. Activation enthalpies as a function of ring size. C_6^* as earlier

more direct effect of the adjacent aromatic ring, or larger steric hindrance of the ring of the α-tetralone, in contrast with the more distant are more easily reacting keto group of β-tetralone.

Dicyclopropyl ketone was studied because of its hindered keto group. In this case the strained nature of the two cyclopropyl groups can be made responsible for the low reaction rates.

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References

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[2] *Gaál, I., B. Matkovics, M. Marik:* Acta Chim. Hung. **75**, 171. (1973).

КИНЕТИЧЕСКОЕ ИЗУЧЕНИЕ РЕАКЦИИ ОБРАЗОВАНИЯ ОКСИМОВ ИЗ КЕТОНОВ

Ч. Конц, Б. Маткович

Изучена кинетика реакции образования оксимов из али-, моно- и бициклических кетонов и проведено сравнение полученных результатов.

Наряду с ранее проводимым титриметрическим методом, проведна попытка спектроскопического изучения кинетики путем наблюдения изменений максимума поглощения салицилата гидроксиламина в ультрафиолетовой области. В данной работе доложено об этих результатах и найдённых возможностях более точного определения кинетических параметров реакции.