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Alkyl Cyanates

X. Kinetics of the Formation of Alkyl Cyanates from 5-Alkoxy-1,2,3,4-thiatriazoles

KAI ARNE JENSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

SVEN BURMESTER

Universidad Nacional de San Cristobal de Huamanga, Ayacucho, Peru

THOR A. BAK

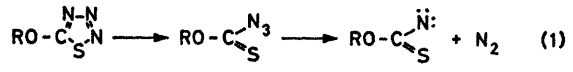
Chemical Laboratory III (General and Theoretical Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

The kinetics of the decomposition of 5-alkoxy-1,2,3,4-thiatriazoles into alkyl cyanates, nitrogen, and sulfur has been investigated in dibutyl phthalate solution by manometric measurement of the nitrogen evolved. The reaction was found to be of the first order. The activation energies for different alkoxythiatriazoles are all about 24.6 kcal·mol^{-1} and the activation entropies are about 4.4 cal·mol^{-1}·°K^{-1}. This is in accordance with the postulated mechanism that the rate-determining step is the breaking of a bond with the formation of a thioazide, which subsequently looses nitrogen and sulfur to form the cyanate. The rate of decomposition of 5-ethoxy-1,2,3,4-thiatriazoles was further studied with the addition of various potential catalysts but practically no catalytic effect was observed.

5-Alkoxy-1,2,3,4-thiatriazoles in dilute solution decompose smoothly at room temperature forming alkyl cyanates, sulfur, and nitrogen.[1] This decomposition is analogous with the decomposition of 5-aryl- or 5-alkyl-1,2,3,4-thiatriazoles into nitriles, sulfur, and nitrogen.[2] In the latter reaction aryl isothiocyanates have been observed as by-products.[3,4] This shows that nitrogen is split off first with the formation of an intermediate R—C(=S)N which may either loose sulfur and form a nitrile or rearrange into the isothiocyanate.

An analogous by-product has not yet been observed in the decomposition of 5-alkoxy-1,2,3,4-thiatriazoles. Isothiocyanates of the type RO—NCS are unknown and our attempts to prepare them from *O*-alkylhydroxylamines and thiophosgene indicate that they may be very unstable.

It is plausible that the first step in the reaction is the opening of the thiatriazole ring with the formation of a thioazide:



(1)

(2)

If this mechanism is correct the thioazide must decompose very rapidly since the characteristic azide band at approximately 2130 cm^{-1} is not observed in the infrared spectrum of a decomposing thiatriazole and furthermore the reaction is kinetically strictly of the first order. We have investigated the kinetics of the decomposition of various 5-alkoxy-1,2,3,4-thiatriazoles (R = methyl, ethyl, propyl, heptyl, and phenyl) by manometric measurements of the nitrogen evolved. Dibutyl phthalate was found to be a convenient solvent in these experiments because it has a negligible vapour pressure at the temperatures used. For the measurements we used the apparatus described by Birkhimer, Norup and Bak [5] with a few minor modifications. The principle of the apparatus is that the evolution of nitrogen produces variations in the height of a mercury column. This in turn is converted into a proportional variation in an electric potential which is recorded on a recording potentiometer. From the experimental data the order of the reaction and the rate constant was obtained by at least squares procedure. The methods of calculation will be treated in detail in a fortcoming paper by K. Andersen.

The reaction was found to be of the first order as mentioned above. The rate constants were determined at various temperatures between 15°C and 40°C and the data was used to calculate the activation energies and activation entropies. The rate constants at 25°C were calculated from the Arrhenius

Table 1. Rates of decomposition of 5-alkoxy-1,2,3,4-thiatriazoles, $RO-CSN_3$. (k_1 = rate constant (25°C), A = Arrhenius factor, $E^{\ddagger}$ = activation energy, $\Delta S^{\ddagger}$ = activation entropy).

R	$k_1(25)$ ($10^{-5}sec^{-1}$)	$t_{\frac{1}{2}}$ (hours)	A ($10^{14}sec^{-1}$)	$E^{\ddagger}$ ($kcal \cdot mol^{-1}$)	$\Delta S^{\ddagger}$ ($cal \cdot mol^{-1} \cdot °K^{-1}$)
CH_3	12.71±0.09	1.52±0.01	1.4±0.3	24.6±0.1	4.2±0.4
C_2H_5	8.95±0.05	2.15±0.01	1.3±0.3	24.8±0.1	4.1±0.4
n-C_3H_7	9.48±0.04	2.03±0.01	1.8±0.3	24.9±0.1	4.7±0.3
n-C_7H_{15}	9.21±0.10	2.09±0.02	1.2±0.4	24.7±0.2	3.9±0.6
C_6H_5	13.13±0.18	1.47±0.02	0.9±0.3	24.3±0.2	3.2±0.6

Table 2. Rate constants, $k_1(10^{-6}sec^{-1})$, for the decomposition of 5-alkoxy-1,2,3,4-thiatriazoles, $RO-CSN_3$, at different temperatures, t (°C).

R = CH_3		R = n-C_3H_7		R = C_2H_5		R = n-C_7H_{15}		R = C_6H_5	
t	k_1	t	k_1	t	k_1	t	k_1	t	k_1
16.77	4.05	18.14	3.44	15.32	2.13	17.35	2.92	17.00	4.11
16.77	3.98	18.15	3.48	15.33	2.15	17.40	3.14	17.00	4.48
16.76	3.79	18.14	3.52	15.32	2.20	25.25	9.62	17.05	4.04
16.75	3.97	25.26	9.37	20.22	4.58	25.27	9.56	25.23	13.5
25.20	13.15	25.21	9.65	20.21	4.42	25.27	9.83	25.21	13.6
25.16	12.69	25.21	9.78	20.20	4.62	32.62	26.7	25.22	13.4
25.17	12.79	25.22	9.74	25.43	9.52	32.60	26.0	32.38	34.8
25.16	13.34	33.00	28.6	25.45	9.62	32.61	24.7	32.39	35.7
32.90	36.9	33.02	28.1	30.25	17.9	32.62	21.6	32.40	35.3
32.91	36.2	33.05	28.2	30.25	18.5	41.55	83.8	32.39	36.1
32.91	37.5	40.44	76.0	30.44	18.6	41.55	84.5	40.28	94.7
40.79	104.5	40.44	76.0	35.30	31.1	41.54	84.1	40.30	94.2
40.80	106.9	40.47	72.9	35.35	37.5	41.50	81.1	40.25	99.1
40.79	101.4			35.34	36.5				
				35.34	36.4				
				35.35	36.8				
				35.41	35.4				
				35.39	34.7				
				35.40	33.4				
				40.29	69.7				
				40.30	69.3				
				40.31	69.3				

equation with a statistical error of 1 % or less (Table 1). The individual data are listed in Table 2.

It is remarkable that the activation energies for the different alkoxythiatriazoles differ very little. This would be consistent with the idea that the reaction proceeds *via* the same mechanism in all cases, the rate-determining reaction being the initial ring-opening process, in which an S—N bond is being broken. The fact that the various substituents influence the rate very little just means that the normal modes fall in two groups which are fairly strongly localized in the thiatriazole ring and in the substituent, respectively.

The entropy of activation, calculated from the equation:

$$k_1 = \frac{ekT}{h} \exp\left(-\frac{E^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}\right)$$

is positive and — within the probable error — identical for all the reactions we have investigated. A positive entropy of activation is in agreement with the postulated mechanism, *i.e.* the transformation of a ring system into an acyclic transition state, but as is well known in itself this does not give strong support to the suggested mechanism.

The rate of decomposition of 5-ethoxy-1,2,3,4-thiatriazole has further been studied with the addition of trichloroacetic acid, tripentylamine, 4-benzylpyridine, anhydrous aluminium chloride, and 1,3,5-trinitrobenzene, to see

whether acids, bases, or Lewis acids (the choice of such compounds was limited because they had to be nonvolatile and soluble in dibutyl phthalate) had a catalytic effect on the decomposition. Practically no effect on the reaction rate was observed (Table 3).

Table 3. Rate of decomposition of 5-ethoxy-1,2,3,4-thiatriazole in the presence of various potential catalysts.

t(°C)	Compounds added	Amount (mg/15 ml)	$k_1(10^{-5}sec^{-1})$
39.81	trichloroacetic acid	70	64.5
40.13	»	140	67.6
40.10	»	280	66.9
40.11	»	560	68.3
40.04	tripentylamine	250	68.9
40.01	»	500	68.9
40.12	4-benzylpyridine	112	68.8
40.12	»	237	67.7
40.15	»	414	68.2
40.14	»	832	71.3
40.14	aluminium chloride	saturated	75.2
40.13	1,3,5-trinitrobenzene	323	68.1

This is rather surprising, because from earlier experiences it was expected that the decomposition of thiatriazoles would be subject to catalytic influence from impurities, as shown by the fact that in undiluted state they sometimes decompose violently and even explosively. However, the explanation of this phenomenon may be that the rather high activation energy causes a very steep increase in the reaction rate with temperature, so that the reaction may

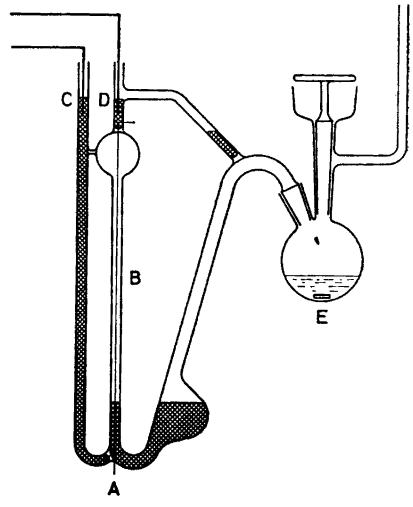


Fig. 1. Mercury filled glass manometer and reaction vessel. A and D are two points between which a platinum resistance wire is stretched. B is the actual manometer. Through the two leads C and D a constant current is sent and the voltage drop over CD is recorded potentiometrically. In the reaction vessel E is seen a glasscovered magnet which is driven by an external magnetic stirrer.

proceed explosively when the temperature is allowed to increase spontaneously. Also, the subsequent isomerisation of cyanates into isocyanates and polymerisation of the latter are strongly exothermic processes and are known to be catalyzed by various catalysts.

EXPERIMENTAL

The 5-alkoxy-1,2,3,4-thiatriazoles were prepared as described in earlier papers from this laboratory.[1] 5-Phenoxy-1,2,3,4-thiatriazole was prepared from phenyl chlorothioformate and sodium azide.[6]

The apparatus used for the measurements was mainly as described by Birkhimer, Norup and Bak.[5] However, the glass apparatus was slightly modified (see Fig. 1) and a voltage stabilizer was used instead of a storage battery. The variations in the potential across the platinum wire was recorded on a Philips *PR 4069M/04* recorder. Otherwise the measurements were carried out as described earlier.[5] About one millimole of the alkoxythiatriazole and 15 ml of dibutylphthalate were used in each experiment. The temperature was kept constant within 0.04°C.

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