THE KINETICS OF THE ADDITION OF GEM-DENITROETHANE TO METHYL ACRYLATE AND ACRYLONITRILE*

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The present paper is devoted to a study of the kinetics of the addition of gem-dinitroethane to methyl acrylate and acrylonitrile in aqueous buffer solutions of variable acidity.[†] The kinetics was studied spectrophotometrically, based on the dinitroethane ion (λ_{max} 380 m μ , log ε 4.23) using an SF-4 instrument. Methyl acrylate, acrylonitrile, and also their addition products with dinitroethane, practically do not absorb in the indicated region (log $\varepsilon \simeq 1$).

EXPERIMENTAL

All of the experiments were run using a large excess of the unsaturated compound, by the change in the concentration of the dinitroethane: a) directly by the decrease in the optical density of the dinitroethane anion (the dinitroethane concentration ranged between approximately 4 and $5 \cdot 10^{-5}$ mole/liter); b) after a 25-100-fold dilution of the reaction solution (dinitroethane concentration ~ $2.5 \cdot 10^{-3}$ mole/liter). The dinitroethane autocondensation product [2] is not formed under the conditions of our experiments (pH 6.80-10.90); the dinitroethane concentration in the buffer solutions does not change for at least two days, whereas the average length of each kinetic experiment was 12 h. Solutions of the reaction products (methyl ester and nitrile‡ of γ , γ -dinitrovaleric acid) fail to show an increase in the optical density with a maximum at 380 m μ in the course of a day, which testifies to the irreversibility of the studied reaction. The rate constants (k₁) were calculated using the first-order equation for irreversible reactions, while the second-order rate constants (k₂) were calculated using the equation k₂ = k₁/c, where c is the concentration of the unsaturated compound. As an example we have given, in the figure, the kinetic curves and their anamorphoses for three experiments. The experimental data are given in Tables 1-3.

The activation energies, calculated from the data given in Table 3, are 14.9 and 17.5 kcal·mole⁻¹ for the reaction of dinitroethane with methyl acrylate and acrylonitrile, respectively.

As can be seen from Tables 1 and 2, the dinitroethane concentration in the separate experiments was varied 60-140 times, while the concentration of the unsaturated compound was varied approximately 3 times. Still we obtained a linear dependence between $\log 1/1 - x$ and t in each experiment (see figure), and also a good agreement of the second-order rate constants in all of the experiments. Since we studied the kinetics under conditions where the dinitroethane (pK 5.21 [4]) was completely ionized, the second-order rate constants given in Tables 1 and 2 are true values. Variation in the hydrogen-ion concentration ~ 1000-10,000 times does not affect the second-order rate constants. Consequently, the determining reaction step is the attack of the β -carbon atom of the unsaturated compound by the dinitroethane anion

^{*}See [1] for preceding communication.

[†] As buffer mixtures we used NaH₂PO₄ + Na₂HPO₄ (pH 6.80); borax + HCl (pH 8.90; borax + KOH (pH 9.50); Na₂CO₃ + HCl (pH 10.90). A constant ionic strength of the solutions was achieved by adding KCl.

[‡]The nitrile was obtained by a procedure similar to the reaction of dinitroethane with methyl acrylate [3]; b. p. 116° (0.7 mm); n_D^{25} 1.4675. Found: N 24.10, 24.22%. $C_5H_7N_3O_4$. Calculated: N 24.27%.



Kinetic curves and their anamorphoses for the experiments: 1) initial DNE concentration $205.14 \cdot 10^{-5}$ mole \cdot liter⁻¹, AN concentration $24.02 \cdot 10^{-2}$ mole \cdot liter⁻¹; 2) initial DNE concentration $170.9 \cdot 10^{-5}$ mole \cdot liter⁻¹, MAC concentration $11.24 \cdot 10^{-2}$ mole \cdot liter⁻¹; 3) initial DNE concentration $4.90 \cdot 10^{-5}$ mole \cdot liter⁻¹, MAC concentration $16.56 \cdot 10^{-2}$ mole \cdot liter⁻¹.

TABLE 1. Rate Constants for the Addition of Dinitroethane (DNE) to Methyl Acrylate (MAC) at 20°

Concentr	ation		· · · ·
DNE, mole · liter ⁻¹ . 10 ⁵	MAC, mole • liter ⁻¹ • 10 ²	^k 1, min ⁻¹ •10 ³	k_2 , liter • mole ⁻¹ • min ⁻¹ • 10 ²
4.30	2.31	0.79	3.42
266.8	12.12	4.35	3.56
4,29	14.66	4.96	3.38
4,98	11.50	3.92	3.41
170,9	11.25	3.96	3.52
177.9	7.84	2.71	3.46
4.81	10.99	3.70	3.37
4.90	16.56	5.67	3.42
5,32	9.94	3.34	3.36
5,23	21.15	7.03	3,32
	Concentr DNE, mole · liter ⁻¹ . 10 ⁵ 4.30 266.8 4.29 4.98 170.9 177.9 4.81 4.90 5.32 5.23	ConcentrationDNE, mole \cdot liter $^{-1} \cdot 10^5$ MAC, mole \cdot liter $^{-1} \cdot 10^2$ 4.302.31266.812.124.2914.664.9811.50170.911.25177.97.844.8110.994.9016.565.329.945.2321.15	ConcentrationDNE, mole \cdot liter $^{-1} \cdot 10^5$ MAC, mole \cdot liter $^{-1} \cdot 10^2$ k_1 , min $^{-1} \cdot 10^3$ 4.302.310.79266.812.124.354.2914.664.964.9811.503.92170.911.253.96177.97.842.714.8110.993.704.9016.565.675.329.943.345.2321.157.03

рН	Concentratio	n		
	DNE, mole•liter ¹ •10 ⁵	AN, mole•liter ⁻¹ •10 ²	k ₁ , min ⁻¹ ·10 ³	k₂, liter∙mole ⁻¹ ∙min ⁻¹ •10 ³
6.80	4.64 205.14	59.60 24.02	5.69 2.36	9.55 9.82
9,50	55 3. 27	26.26	2.53	9.64
10.90	4.12 3.90	65.75 44.80	6 .3 4 4 . 29	9.64 9.58

TABLE 2.	Rate Constants	for the	Addition	of Dinitroethane	(DNE) to	Acryl	onitrile	(AN) at 2	20°
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IABLE	S. Rate Constant	s at various 1	emperatures				
Temp., °C	k₂, liter∙mole	$1 \cdot \min^{-1} \cdot 10^2$	Temn	k_2 , liter \cdot mole ⁻¹ \cdot min ⁻¹ \cdot 10 ²			
	DNE + MAC	DNE + AN	°C	DNE + MAC	DNE + AN		
20 25	3.44±0.12 5.41±0.04	0.97±0.01 1.67±0.02	30 40	8.07±0.04 17.80±0.2	2.61±0.01 6.74±0.06		
	[CH₃C(NO	(2)2] + CH2=C	(slow) CHR → CH3-	NO₂ −C−CH₂CHR ↓ NO₂			
	NC CH3 —C— NC	C_2 -CH ₂ - \overline{C} HR +	$\begin{array}{cc} (\text{fast}) & \\ \\ - & H^+ \rightarrow CH_3C \\ \\ N \end{array}$	O₂ C—CH₂CH₂R O₂			

TABLE 3. Rate Constants at Various Temperatures

This is in agreement with the mechanism proposed by Ingold [5] for the Michael reaction. On the basis of the kinetic data the authors of a number of papers [6] give preference to the same mechanism. From a comparison of the rate constants it follows that the reactivity of methyl acrylate is greater than the reactivity of acrylonitrile. A similar order in the reactivity was also observed in the reaction with trinitromethane [1].

SUMMARY

A study was made of the rate of addition of dinitroethane to methyl acrylate and acrylonitrile. The limiting reaction step is the attack of the β -carbon atom of the unsaturated compound by the dinitroethane anion.

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