## MECHANISM OF THE REACTION OF QUINOBROMIDE COMPOUNDS WITH AMINES

A. A. Volod'kin, D. Kh. Rasuleva,
V. V. Ershov, A. I. Prokof'ev,
S. P. Solodovnikov, N. N. Bubnov,
and S. G. Kukes

A study of the mechanism of the reaction of quinobromide compounds (bromocyclohexadienones) with nucleophilic agents is part of a study of organic reactions involving one electron [1]. The reaction of quinobromide compounds with amines is a convenient model for studying the elementary acts of the process and determining the effect of various factors on the kinetic parameters. Thus, phenoxyl radicals, quin-amines and a number of other compounds are obtained when quinobromide compounds are reacted with amines, in which connection their formation could be explained as being due both to the simultaneous progress of parallel reactions and the successive transformation of the biradical "cage," which is formed as the result of the initial transfer of an electron from the nucleophile to the quinobromide [2]

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The kinetic data of the present paper are in good agreement with the one radical mechanism for the reaction of quinobromide compounds with amines and corroborate the hypothesis of the determining role played by the transfer of one electron in the elementary act of this process. The kinetic measurements were made by two methods: by the accumulation of amine hydrobromide (method A) and of the phenyl radical (method B), the use of which made it possible to determine the effective rate constant for the reaction of quinobromides with amines ( $k_1$ ) and the rate constant for the formation of phenyl radicals ( $k_2$ ), and to

Amine	Solvent	k <sub>1</sub> •10 <sup>3</sup> , liter ∕M• min	Amine	Solvent	k <sub>1</sub> • 10 <sup>3</sup> , liter /M• min	
Morpholine	CCl <sub>4</sub>	6,1	Diisopropy1-	Benzene	2,3	
π	Heptane	5,5	tert:-Butyl-		0,4	
81	Benzene	6,1	Diethvlamine		19,0	
	THF Dioxane	15,0 18,0	Triethylamine Piperidine	n 11	$45.0 \\ 43.0$	

TABLE 1. Rate Constants for Reaction of 4-Bromo-4-methyl-2, 6di-tert-butyl-2, 5-cyclohexadienone with Amines in Various Solvents at 40°C

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Fig. 1. Relative reaction rate of (I) with morpholine as a function of the concentration of the quinobromide (1) and the amine (2). Benzene,  $40^{\circ}$ C.

Fig. 2. Kinetic curve (1) and its semilogarithmic anamorphosis (2) for the reaction of (I) with morpholine. [Quinobromide] = 0.195 M/liter, [morpholine] = 3.2 M/liter, benzene,  $40^{\circ}$ .

TABLE 2. Rate Constants, Preexponential Factors, Activation Energies, and Yields of Quinamines in the Reaction of 4-Bromo-2,4,6-tri-tert-butyl-2,5-cyclohexadienone with Amines (in Benzene)

Method	Amine	k <sub>40</sub> ° • 10 <sup>4</sup> , liter/M • min	k <sub>0</sub> , liter/M • min	E, kcal/M	(1—φ) 100	Yield <sup>*</sup> of quinamine, 1%
А	Morpho-	28	8.107	$15,1\pm0,5$	93	85
B	Piperim	1,9 18	7,2.107	$16,8\pm0,5$ $16,7\pm0,5$		
В	dine	12	1,2.109	$10, 7\pm 0, 5$ $17, 2\pm 0, 5$	33	12
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**From** [2].

estimate the probability of the radicals escaping from the cage that is formed after cleaving HBr from the molecules of the quinobromide and the amine.

The linear character of the relative reaction rate of 4-bromo-4-methyl-2, 6-di-tert-butyl-2, 5-cyclohexadienone (I) with morpholine as a function of the concentration of these components (Fig. 1) testifies to the first order of the reaction in each component. Fig. 2 shows a typical kinetic curve for the reaction of quinobromide (I) in excess morpholine and its semilogarithmic anamorphosis. From the slope of the straight line the bimolecular rate constant  $k_1$  was calculated. The rate constant for the reaction of quinobromide (I) with morpholine increases slightly with increase in the solvating capacity of the solvent and is quite dependent on the nature of the amine (Table 1). In the example of the reaction of quinobromide (I) with diethylamine and its nitrogendeuterated analog \* it was shown that the isotope effect is not detected in this reaction.

The kinetics of the reaction of 4-bromo-2,4,6-tri-tert-butyl-2,5-cyclohexadienone (II) with morpholine and pipericine (in benzene) was studied on the basis of the accumulation of the amine hydrobromide and 2,4,6-tri-tert-butylphenoxyl (III). Since phenoxyl (III) reacts with amines [3], but at a much slower rate, then the rate based on radical (III) was determined from the initial linear section of the kinetic curve. In Table 2 are given the kinetic parameters for the reaction of quinobromide (II) with amines, which were calculated using methods A and B. A divergence in the values of the rate constants and activation energies

\*Based on the IR spectrum the enrichment of the sample was 85-90%.

for the reaction of quinobromide (II) with morpholine (and piperidine) is associated with the fact that phenoxyl (III) is a secondary reaction product and is formed only in the case of the radicals escaping from the cage. If the probability of escape from the cage is taken as equal to  $\varphi$ , then the formation of radical (III) should proceed with a constant of  $k_1 \varphi$ . In harmony with this, the quantity  $(1-\varphi)$  should correspond to the yield of the quinamines, which actually does correspond to the experimental data [2]. A difference of 1-2 kcal /M in the values of the activation energy for the same reaction, but determined by different methods, can be attributed to the diffusion of the radicals from the cage.

## EXPERIMENTAL METHOD

The kinetic measurements relative to the amine hydrobromide were run in thermostatted test tubes, and the amount of salt was determined by weighing. The error of the method did not exceed 15%. The kinetic measurements on the change in the concentration of 2,4,6-tri-tert-butylphenoxyl were run on a RÉ-1301 spectrophotometer in evacuated ampuls [4].

## CONCLUSIONS

The mechanism of the reaction of quinobromide compounds with amines was studied by the kinetic method.

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