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Ignazio Renato Bellobono, Gian Marco Sabbadini

Nucleophilic substitution of a nitro-group in polymtrobenzenes. III. - Kinetics of the reaction of 1, 2-dinitrobenzene with methoxide ion in methanol solution

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Chimica fisica. — *Nucleophilic substitution of a nitro-group in polynitrobenzenes.* III. – *Kinetics of the reaction of 1, 2-dinitrobenzene with methoxide ion in methanol solution* (*). Nota di IGNAZIO RENATO BELLOBONO e GIAN MARCO SABBADINI, presentata (**) dal Corrisp. M. SIMONETTA.

RIASSUNTO. — La cinetica della reazione tra 1,2-dinitrobenzene e metossido di sodio in soluzione metanolica per dare *o*-nitroanisolo è stata seguita a 15,1, 25,0, e 40,0° C. I coefficienti cinetici di pseudo primo ordine sono stati trovati in correlazione lineare non con la concentrazione dell'alcossido (nell'intervallo 0,25–1,24 M), bensì con l'attività dello ione metossido. Si sono potute così ottenere in modo consistente costanti cinetiche bimolecolari.

1. – INTRODUCTION.

Kinetics of the reaction between 1,2-dinitrobenzene and methoxide ion in methanol solution to yield *o*-nitroanisole and nitrite ion was first investigated by Lobry de Bruyn and Steger [1–3], and more recently by Tommila and Murto [4], in connection with the studies of these latter Authors on the influence of solvent (methanol, ethanol, and water-alcohol mixtures) on reaction velocity. The *o*-dinitrobenzene was found to react more slowly than the *para*-isomeride in anhydrous alcohol. The influence of methoxide concentration on reaction rate was systematically examined, only at 20° C, by Schaal and Latour [5]. As for the case of 1,4-dinitrobenzene, pseudo-first order rate constants (k_I) were found to be correlated not with concentration of alkoxide, but with Hammett function H_M defined for concentrated methoxide solutions by:

$$H_M = -\log a_{CH_3OH_2^+} \frac{f_{A^-}}{f_{AH}}$$

where $a_{CH_3OH_2^+}$ is the activity of $CH_3OH_2^+$ ion and f are molar activity coefficients of the acid-base couples (AH/A^-) which were used to determine the Hammett function H_M. A linear relation between $\log k_I$ and H_M was in fact observed.

In a previous paper [6], kinetic data relative to the nucleophilic substitution of a nitro-group in 1,4-dinitrobenzene by methoxide ion in methanol

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solution were found to give consistent bimolecular rate constants, when using activities of methoxide ion instead of concentrations.

The same treatment is now extended to the similar reaction of the *ortho*-isomeride.

2. – EXPERIMENTAL.

2.1. – *Materials*.

Reagent grade 1,2–dinitrobenzene was recrystallized from methyl alcohol to constant melting point (m.p. 118° C).

Anhydrous methanol and sodium methoxide solutions were prepared as previously described [7].

TABLE I.

Pseudo-first order rate constants for the nucleophilic substitution of a nitro-group in 1,2–dinitrobenzene by methoxide ion in methanol solution.

Sodium methoxide concentration (M)	k_1 ($M^{-1} s^{-1}$)		
	15.1° C	25.0° C	40.0° C
0.259	—	—	1.72×10^{-4}
0.327	—	—	2.07×10^{-4}
0.460	—	—	3.42×10^{-4}
0.560	—	—	4.84×10^{-4}
0.647	—	1.48×10^{-4}	—
0.661	—	—	7.31×10^{-4}
0.711	—	—	8.66×10^{-4}
0.785	—	2.63×10^{-4}	—
0.792	8.89×10^{-5}	—	—
0.852	9.40×10^{-5}	—	—
0.921	1.23×10^{-4}	—	—
0.939	—	3.51×10^{-4}	—
0.995	—	3.56×10^{-4}	—
1.075	1.59×10^{-4}	—	—
1.095	—	4.18×10^{-4}	—
1.109	—	4.45×10^{-4}	—
1.196	2.04×10^{-4}	—	—
1.239	—	4.16×10^{-4}	—

2.2. – *Kinetics.*

Solutions of 1,2–dinitrobenzene and sodium methoxide in anhydrous methanol were thermostated separately and mixed for kinetic measurements. Concentrations after mixing were 6.05×10^{-5} M and 0.25–1.24 M respectively.

Reaction vessels were protected from light and thermostated at 15.1, 25.0 and 40.0 °C. Samples were removed and analyzed spectrophotometrically by a Beckman DU apparatus, equipped with a thermostated cell compartment (constancy of temperature within $\pm 0.05^{\circ}$ C). Increase of absorbance at 320 nm, due to formation of *o*–nitroanisole [5] was followed as a function of time. The pseudo-first order constant k_{I} was obtained by plots of $\log (A_{\infty} - A_t)$ vs. t, where A are the absorbances at t or infinite time. The plots were linear up to 85–90 % reaction. Experimental results are collected in Table I.

3. – RESULTS AND DISCUSSION.

Kinetics of reaction between 1,2–dinitrobenzene and sodium methoxide in methanol solution was measured with the same initial concentration of the nitro-compound (6.05×10^{-5}M) in all runs and variable concentrations of alkoxide (0.25–1.24M), at 15.1, 25.0, and 40.0° C, by spectrophotometric

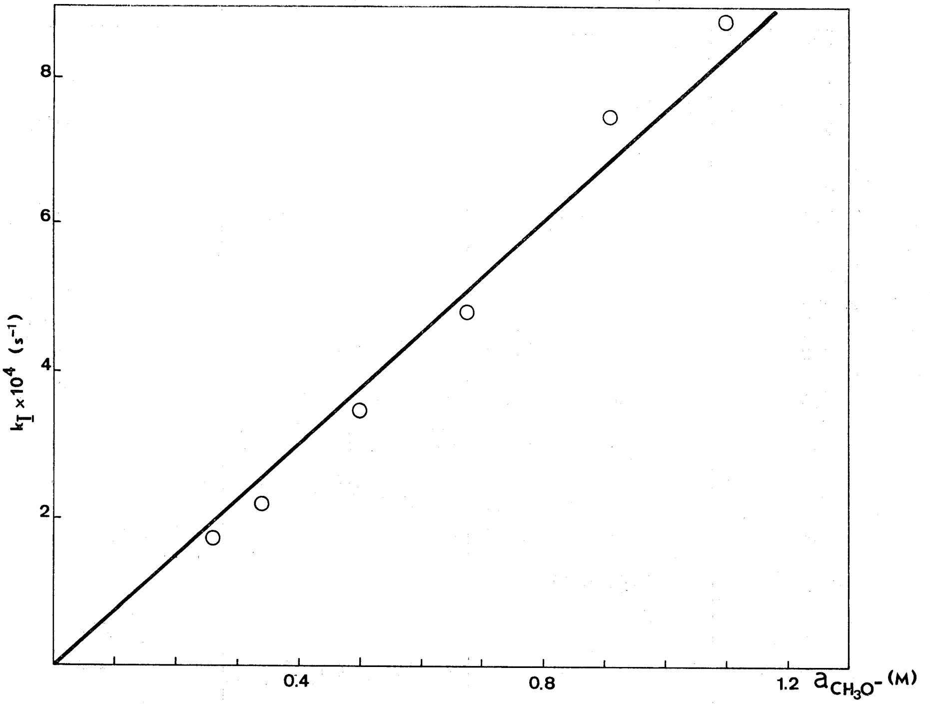

Fig. 1. – Pseudo-first order rate constants for the nucleophilic substitution of a nitro-group in 1,2–dinitrobenzene at 40.0° C, by methoxide ion in methanol solution, as a function of methoxide ion activity.

analysis of the rate of formation of the product (*o*–nitroanisole). As for the case of 1,4–dinitrobenzene, in the experimental conditions employed reaction occurred in absence of measurable concentration of any sodium methoxide addition complex. Observed pseudo-first order rate constants (Table I) were not a linear function of methoxide concentration. A fairly satisfactory linearity was instead exhibited by plots of k_I vs. activity of methoxide ion, this latter being evaluated by the same method described for the similar reaction of *p*–dinitrobenzene [6]. An example of such plots is shown in fig. 1. From these plots consistent values of the second order

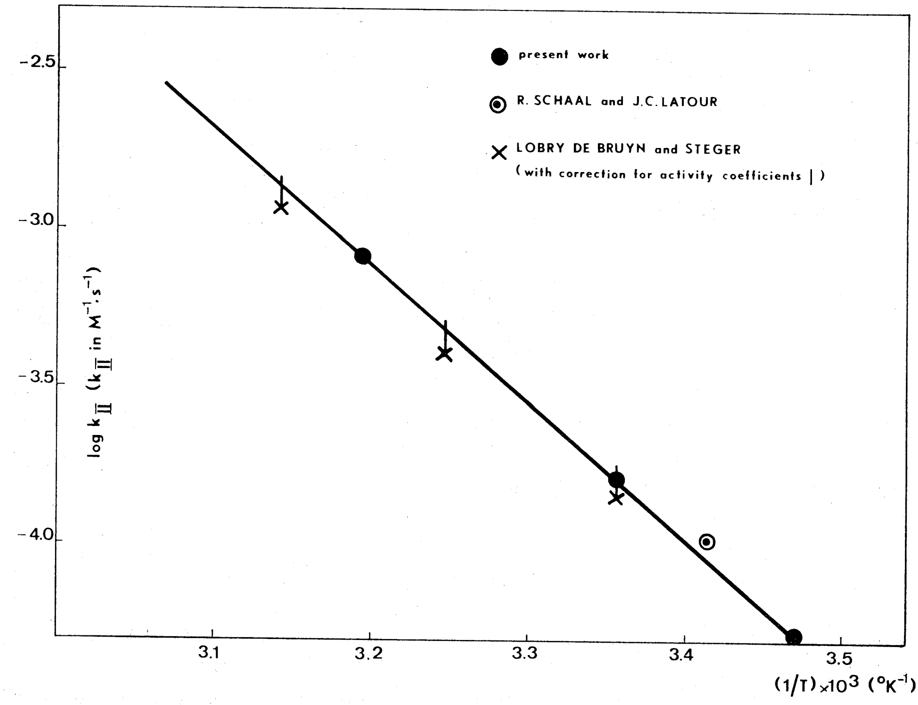

Fig. 2. – Arrhenius plot of bimolecular rate constants for the nucleophilic substitution of a nitro-group in 1,2–dinitrobenzene by methoxide ion in methanol solution.

rate constants could be obtained. They are reported in Table II, together with the value calculated from literature data [5] at 20° C. All values are corrected for thermal expansion of solutions at the temperatures at which kinetics were run. The value at 20° C and those measured in the present paper fit the Arrhenius plot (fig. 2) quite satisfactorily. In fig. 2 the values of the second order rate constants relative to experiments by Lobry de Bruyn and Steger [1–3] (see reference [4]) are also reported, with a correction of about 0.12 in log k_{II} (shown by a dash), including the effect of activity coefficients of methoxide ion (see reference [6]) at a concentration of 5×10^{-2} M as employed by the cited Authors. These corrected values show a better correlation with the present measurements than the uncorrected ones. Taking into account all experimental data available, the activation energy ($\Delta E^{\ddagger} = 19.9$ Kcal/gmole) and the frequency factor ($\log A = 11.20$, A in $M^{-1}\,s^{-1}$) can be calculated.

TABLE II.

Second order rate constants for nucleophilic substitution of a nitro-group in 1,2–dinitrobenzene by methoxide ion in methanol solution.

Temperature (°C)	k_{II} ($M^{-1}\,s^{-1}$)
15.1	5.56×10^{-5}
20.0	9.76×10^{-5} (a)
25.0	1.49×10^{-4}
40.0	7.98×10^{-4}

(a) value calculated by the $k_I/a_{CH_3O^-}$ plot from k_I data of reference [5].

It may be emphasized that reaction of 1,2–dinitrobenzene with methoxide ion, similarly to that of the *para*–isomeride and to the more complex case of 1,3,5–trinitrobenzene, can be conveniently interpreted in terms of activities of methoxide ions, which allow to obtain consistent bimolecular rate constants over a very wide range of methoxide concentrations, despite some approximations involved in this type of treatment.

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