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Communications to the Editor

Pyrolysis of Alkyl Nitrites (RONO)

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It has been established via $\Delta H_f^\circ(\mathrm{RONO})$ and $\Delta H_f^\circ(\mathrm{R\dot{O}})$ that $\Delta H_{1,2}^\circ = 41.5 \pm 1$ kcal/mole [1]. Assuming that $E_2 = \mathrm{O}$,

$$(2) \qquad \mathrm{RONO} \rightleftarrows \mathrm{R\dot{O}} + \mathrm{NO} \qquad (1)^{1}$$

$\Delta H_{1,2}^\circ$ may also be identified with the RO—NO bond dissociation energy. However, gas-phase kinetic studies have indicated that $E_1 = 37 \pm 1$ kcal/mole [2], incompatible with the above. Our recent kinetic studies on the decomposition of RONO show that the apparent disagreement between the kinetic and thermochemical data can be resolved in terms of the effect of two parallel reactions: a homogeneous radical split and either a homogeneous or a heterogeneous molecular elimination process.

The object of this study has been to isolate and follow the rate of breaking of the RO—NO bond using a conventional static system over the temperature range 120–200°C. For R = *t*-Bu, *i*-Pr, and Et, this has been achieved by using low concentrations of nitrite (10^{-5}–10^{-4} *M*) with a high total pressure of $\mathrm{CF_4}$ (~0.9 atm) and small extents of reaction (~1%). Under these conditions the first-order homogeneous rates of acetone, acetaldehyde, or formaldehyde formation are a direct measure of reaction (1),

$$(2) \qquad \mathrm{RONO} \rightleftarrows \mathrm{R\dot{O}} + \mathrm{NO} \qquad (1)$$

$$\mathrm{R\dot{O}} \rightarrow \text{products} \qquad (3)$$

since k_3 [3] $\gg k_2(\mathrm{NO})$. These rates are very much less in the absence of $\mathrm{CF_4}$. For R = Me, isobutane is used as a radical trap:

$$\mathrm{Me\dot{O}} + t\text{-BuH} \rightarrow \mathrm{MeOH} + t\text{-}\dot{\mathrm{B}}\mathrm{u} \qquad (4)$$

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[1] In this paper the following convention is used. The reaction AB → A + B (1) has a rate coefficient given by $k_1 = A_1 e^{-E_1/RT}$. The reverse reaction A + B → AB (2) has a rate coefficient given by $k_2 = A_2 e^{-E_2/RT}$. E_1 and E_2 are related by $E_1 - E_2 = \Delta \mathrm{H}_{1,2}^\circ - RT$ or $E_2 - E_1 = \Delta H_{2,1}^\circ + RT$. $\Delta H_{1,2}^\circ = \Delta H_f^\circ(\mathrm{A}) + \Delta H_f^\circ(\mathrm{B}) - \Delta H_f^\circ(\mathrm{AB})$. Similarly $\Delta S_{1,2}^\circ = S_{\mathrm{A}}^\circ + S_{\mathrm{B}}^\circ - S_{\mathrm{AB}}^\circ$. Finally the equilibrium constant $K_{1,2}$ for the equilibrium (2) AB $\rightleftarrows$ A + B (1) is defined by $K_{1,2} = k_1/k_2$ whereas $K_{2,1} = k_2/k_1$.

and the methanol formed again gives a direct measure of reaction (1). In all four cases, the addition of large amounts of NO, in place of CF_4 or isobutane, almost completely supresses ketone, aldehyde, or methanol formation, verifying that these products are indeed a measure of the radical split (1).

Thermochemical and kinetic data for RONO are given in Table I. Kinetic values for $D(\text{RO—NO}) = E_1 + RT$ are now in complete harmony with $\Delta H_{1,2}°$ (298°K). This verifies the assumptions that $D(\text{RO—NO}) = 41.5 \pm 1$ kcal/mole and that $E_2 = \text{O} \pm 1$ kcal/mole. Another feature of this study is that the values for the preexponential factors A_1 (Table I) are much higher than those previously quoted ($10^{13.5\pm1}$ sec^{-1}) which had been regarded as "suspiciously low" [4]. We expect most if not all processes splitting into two groups (other than a light atom like H) to have preexponential factors of this order of magnitude. These values imply that the RO—NO bond is lengthened by a factor of ~2.5 in the transition state [4]. From $\Delta S_{1,2}°$ (Table I) values for A_2 and hence k_2, since $E_2 = \text{O}$, have been calculated to be $\sim 10^{10.3}$ M^{-1} sec^{-1}. In terms of simple collision theory, this means that combination occurs once every ten collisions. These values for k_2 are three powers of ten higher than those previously quoted.

For R = Me, Et, or *i*-Pr first-order (in a spherical R.V.) heterogeneous elimination of HNO occurs:

$$\begin{aligned} &\text{MeONO} \rightarrow CH_2O + \text{HNO} \\ &\text{EtONO} \rightarrow CH_3CHO + \text{HNO} \qquad (5) \\ &i\text{-PrONO} \rightarrow CH_3COCH_3 + \text{HNO} \end{aligned}$$

Table I. Thermochemical and kinetic data for RONO.

R	log A_1 (sec^{-1}) ($\pm$ 0.4)	$\Delta S^{\circ}_{1,2}$ (gibbs mole^{-1}) ($\pm$ 1)	log A_2 (M^{-1} sec^{-1}) ($\pm$ 0.4)	E_1 (Kcal mole^{-1})	$\Delta H^{\circ}_{1,2}$ (Kcal mole^{-1})
Me	15.8	34.7	10.1	41.2 $\pm$ 1	41.8 $\pm$ 0.9
Et	16.0	34.8	10.3	41.8 $\pm$ 0.9	42.0 $\pm$ 1.3
i-Pr	16.2	35.0	10.4	41.0 $\pm$ 0.8	41.0 $\pm$ 1.3
t-Bu	16.3	35.6	10.4	40.3 $\pm$ 0.8	41.1 $\pm$ 1.3

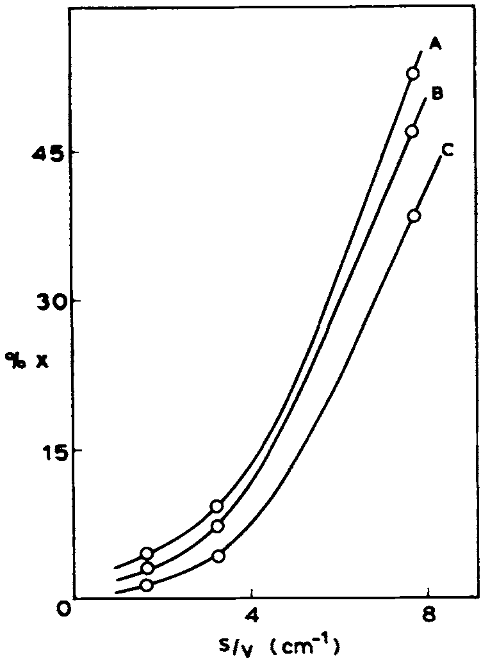

Figure 1. Effect of changing S/V of R.V.S. as a function of HNO for RONO. A—MeONO, X = CH_2O; B—EtONO, X = CH_3CHO; C—i-PrONO, X = CH_3COCH_3.

Figure 1 shows the effect of changing the ratio S/V, for different reaction vessels, on the rate of these reactions. Addition of NO enhances the rate of these reactions. They were probably obscured in previous studies because these involved large extents of reaction, and disproportionation took place between $R\dot{O}$ and NO at relatively high NO concentrations; such as reaction (6):

$$CH_3\dot{O} + NO \rightarrow CH_2O + HNO \tag{6}$$

Incidentally, our studies also show that k_2/k_6 is essentially temperature independent, that is, $E_6 = O \pm 1$ kcal/mole. When R = t-Bu, the parallel reaction is the first-order homogeneous elimination of HONO:

$$t\text{-BuONO} \rightarrow Me_2C = CH_2 + HONO \tag{7}$$

The rate of this reaction is unaffected by the addition of NO. The participation of these reactions resulted in a lowering of the observed Arrhenius parameters in previous studies. This is illustrated by the Arrhenius plots for t-BuONO in Figure 2. Table II gives the Arrhenius parameters for these reactions. In particular, $k_{\text{global}} = 10^{14.7}\ 10^{-36.2/\theta}\ \text{sec}^{-1}$, a value similar to previous results for RONO [2].

TABLE II. Kinetic data for *t*-BuONO.

Process	log A sec^{-1} ($\pm$ 0.4)	E Kcal $mole^{-1}$ ($\pm$ 0.8)
(1)	16.3	40.3
(7)	12.9	33.6
(1) + (7)	14.7	36.2

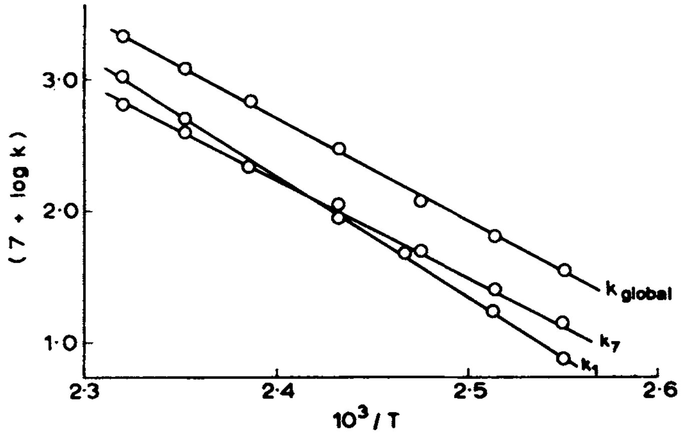

Figure 2. Arrhenius plots for *t*-BuONO.

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