Addition Reaction with 2-Methyl-2-nitrosopropane and Pressure Dependence of Ionized Picoline *N*-Oxides in the Gas Phase

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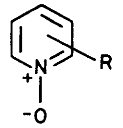
The equilibrium of the addition reaction of ionized picoline *N*-oxides with 2-methyl-2-nitrosopropane as an ion-trapping reagent was determined at various temperatures in the gas phase. From the thermodynamic properties of the addition reaction, the structures of the addition products are discussed. In connection with the addition reaction, the pressure dependence of the mass spectra of picoline *N*-oxides is discussed, and it is concluded that the pressure dependence is caused by the effect of the charge transfer reaction between the $(M - O)^+$ species and a neutral molecule of picoline *N*-oxide through an intermediate ion $(M_2 - O)^+$. Upon the formation of this intermediate ion, picoline *N*-oxides acted as ion-trapping reagents in a similar manner to 2-methyl-2-nitrosopropane.

IN previous studies of the mass spectra of nitrogen-containing heteroaromatic *N*-oxides, hydroxylimino-compounds, and azoxy-compounds, the relative abundances of the $(M - O)^+$ species formed by the elimination of an oxygen atom from the molecular ion depended greatly upon the pressure of the sample. The relative abundances were larger at the lower sample pressures and smaller at the higher.[1] In these studies, we found that the pressure dependence was characteristic for the fragmentation of species with a co-ordinate N–O bond, but we could not establish what kinds of interaction act on the dissociation of the ionized molecule in the gas phase. The pressure dependence was also observed in the mass spectra of pyridine derivatives, indicating the influence of the formation of secondary ions.[2] We studied the mass spectra of some nitroso-compounds and found that they were useful as ion-trapping reagents to detect short-lived intermediate ions and to study the thermodynamic properties of ionized molecules in the gas phase. We have applied this method to various kinds of gaseous organic ions. For a study of the addition reaction of aliphatic alcohol ions with 2-methyl-2-nitrosopropane (Bu^tNO), we believe that the structure and the thermodynamic properties of addition products are a function of alkyl chain length of the alcohol.

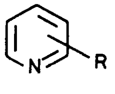
In this study, we describe the addition reaction of ionized picoline *N*-oxides with Bu^tNO and discuss the pressure dependence of their mass spectra.

RESULTS AND DISCUSSION

The addition products discussed in this paper are $M^{+\bullet}Bu^tNO$ and $(M - O)^{+\bullet}Bu^tNO$ in the case of (I) and also $M^{+\bullet}Bu^tNO$ in the case of (II) where M^+ is the molecular ion. The formation reactions of these ions are



(I)



(II)

a; R = 2-Me
b; R = 3-Me
c; R = 4-Me

expressed by equations (1). From reaction (1), the

$$A^+ + Bu^tNO \rightleftharpoons A^{+\bullet}Bu^tN\dot{O} \quad (1)$$

$$A^+ = (CH_3C_5H_4N{-}O)^+,\ M^+ \text{ of (I)} \quad (1a)$$

$$A^+ = (CH_3C_5H_4N)^+,\ (M - O)^+ \text{ of (I)} \quad (1b)$$

$$A^+ = (CH_3C_5H_4N)^+,\ M^+ \text{ of (II)} \quad (1c)$$

expression for the equilibrium constant K_p is given by equation (2) where P and I represent the partial pressures and the ion intensities. The value of α is 1.12 given by the slope of the ion intensity–pressure curve. The van't Hoff plots of equilibrium constant data for reactions (1a—c) are shown in Figures 1—3. The values of $\Delta H°$ of reaction (1) are calculated from the slope of straight lines of van't Hoff plots by the least-squares treatment. The values of $\Delta H°$, $\Delta G°$, and $\Delta S°$ of reaction (1) for each compound are shown in Table 1.

$$K_p(1) = \frac{1}{P_{Bu^tNO}} \frac{P_{A^{+\bullet}Bu^tNO}}{P_{A^+}} = \frac{1}{P_{Bu^tNO}} \left(\frac{I_{A^{+\bullet}Bu^tNO}}{I_{A^+}}\right)^{\alpha} \quad (2)$$

TABLE 1

The values of $\Delta H°$, $\Delta G°$, and $\Delta S°$ of reaction (1)

Reaction	Compd.	$\Delta H°$ (1)/ kJ mol^{-1}	$\Delta G°$ (1)/ kJ mol^{-1}	$\Delta S°$ (1)/ J mol^{-1} K^{-1}
(1a)	(Ia)	−69.4	−46.0	−78.6
(1a)	(Ib)	−68.1	−45.1	−77.3
(1a)	(Ic)	−69.0	−52.7	−54.8
(1b)	(Ia)	−80.7	−55.5	−84.0
(1b)	(Ib)	−64.4	−52.3	−40.5
(1b)	(Ic)	−69.0	−58.5	−35.1
(1c)	(IIa)	−70.6	−54.3	−54.8
(1c)	(IIb)	−55.2	−49.7	−18.4
(1c)	(IIc)	−58.9	−51.4	−25.1

Standard state; 1 atm and 298 K, experimental error ±8%.

As shown in Table 1, the values of $\Delta H°$ and $\Delta G°$ for reaction (1a) of (I) are constant at *ca.* −69.0 and −48.1 kJ mol^{-1}. It seems that the structures of the addition products formed by reaction (1a) are $[CH_3{-}C_5H_4NO{-}N(O){-}Bu^t]^+$ (a) and $[ON{-}C_5H_4{-}CH_2{-}N(OH){-}Bu^t]^+$ (b). The bond enthalpy changes for the formations of the (a) and (b) types of addition products are −130.8 and 33.9 kJ mol^{-1}, calculated by the neutral-species model.[3] It shows that *ca.* 60% of addition products have the (a) type of structure. Similar structures were reported from spin-trapping studies of heterocyclic compounds

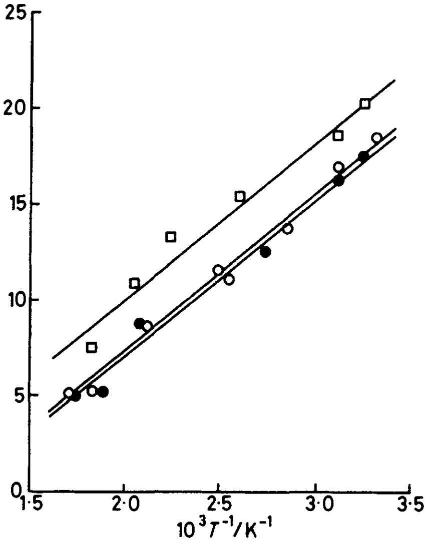


FIGURE 1 van't Hoff plots for reaction (1a): standard state, 1 atm, ○, 2-methylpyridine 1-oxide (Ia); ●, 3-methylpyridine 1-oxide (Ib); □, 4-methylpyridine 1-oxide (Ic)

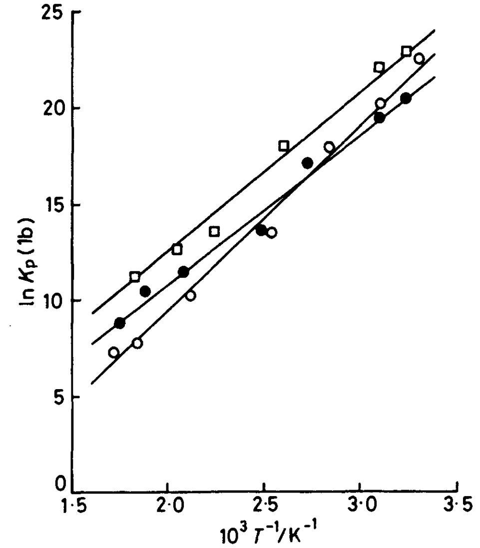


FIGURE 2 van't Hoff plots for reaction (1b): standard state, 1 atm, ○, 2-methylpyridine 1-oxide (Ia); ●, 3-methylpyridine 1-oxide (Ib); □, 4-methylpyridine 1-oxide (Ic)

involving the abstraction of a hydrogen atom or halogen radical.[4-6] The values of $\Delta H°$ and $\Delta G°$ for reaction (1b) of (I) are nearly equal to those for reaction (1c) of (II). It is reasonable that the structures of $(M - O)^+$ of (Ia—c) are same to those of M^+ of (IIa—c), respectively. The values of $-\Delta H°$ for reaction (1b) of (Ia) and that for reaction (1c) of (IIa) are larger by *ca.* 13.8 kJ mol^{-1} in comparison with those for reactions (1b) of (Ib and c), and also with those for reaction (1c) of (IIb and c). This difference for $\Delta H°$ originated from the position of the methyl group in the pyridine ring, *i.e.* from the effect of hydrogen-bond formation between the oxygen atom of the nitroso-group and the hydrogen atom in the 2-methyl group in reaction (1b) of (Ia) and reaction (1c) of (IIa). From these thermodynamic values, the most likely structures of the addition products formed by reactions (1b and c) are $[\mathrm{CH_3{-}C_5H_4N{-}N(O){-}Bu^t}]^+$ (c) and $[\mathrm{NC_5H_4{-}CH_2{-}N(OH){-}Bu^t}]^+$ (d), and also the hydrogen-bonded species $[\mathrm{H{-}CH_2{-}C_5H_4N{-}N(O){-}Bu^t}]^+$ (e) in reaction (1b) of (Ia) and reaction (1c) of (IIa). The bond enthalpy changes for the formations of the (c) and (d) types of addition products are —147.1 and 33.9 kJ mol^{-1} calculated by the neutral-species model. It shows that *ca.* 50—65% of addition products formed by reaction (1b and c) take the (c) type of structure.

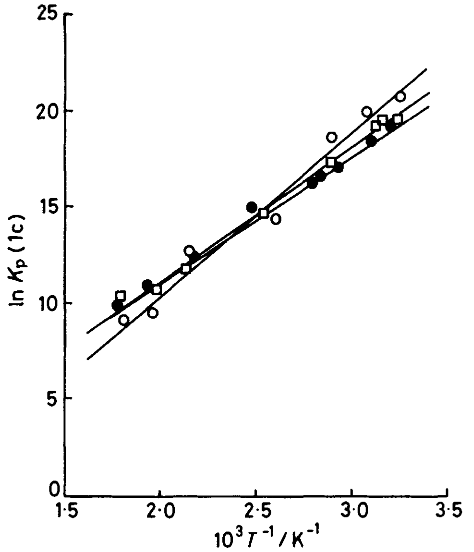


FIGURE 3 van't Hoff plots for reaction (1c): standard state, 1 atm, ○, 2-methylpyridine (IIa); ●, 3-methylpyridine (IIb); □, 4-methylpyridine (IIc)

In the course of our study of the picoline *N*-oxide-Bu^{t}NO system, the secondary ion formulated as the $(M_2 - O)^+$ species was found together with the addition products mentioned above. But the ion abundances of the $(M_2 - O)^+$ species were too small to study the thermodynamic properties quantitatively. Therefore, we re-examined the mass spectral data of picoline *N*-oxides observed under the various sample pressures.[1c] It is possible to consider that the $(M_2 - O)^+$ species of (I) is an activated complex acting as an intermediate in reaction (3). From reaction (3), the expression for the equilibrium constant K_p is (4) where P, I, and α represent the

$$M + (M - O)^+ \rightleftharpoons [(M_2 - O)^+] \rightleftharpoons M^+ + (M - O) \quad (3)$$

$$K_p(3) = \frac{P_{M^+} \cdot P_{(M-O)}}{P_M \cdot P_{(M-O)^+}} = \left[\frac{P_{(M-O)^+}}{P_{M^+}}\right]^{-1} \cdot \frac{P_M{}^{\beta}}{P_M} = \left[\frac{I_{(M-O)^+}}{I_{M^+}}\right]^{-\alpha} \cdot P_M{}^{(\beta-1)} \quad (4)$$

partial pressures, ion intensities, and the ion intensity–pressure coefficient, respectively. β is the pressure coefficient represented by the relation $P_{(M-O)} = P_M{}^{\beta}$. On the assumption that $K_p(3)$ is constant at various sample pressures, the value of $\alpha^{-1}(\beta - 1)$ is given from the slope of straight lines of the logarithm of the relative ion abundance *versus* the sample pressure curve by a least-squares treatment. The values of β for (Ia—c) are 0.90, 0.92, and 0.80, respectively.[1c] The values of ΔG° for reaction (3) are calculated from those of $K_p(3)$ in equation (4) and are shown in Table 2. The values of ΔG° for reactions (1a—c) at 473 K are also shown in Table 2.

TABLE 2

The values of ΔG° for reactions (3) and (1)

Compd.	ΔG° (3)	ΔG° (1a)	ΔG° (1b)	ΔG° (1c)
(Ia)	−11.7	−32.2	−41.0	
(Ib)	−12.1	−31.5	−45.2	
(Ic)	−17.6	−43.1	−52.4	
(IIa)				−44.7
(IIb)				−46.5
(IIc)				−47.1

All values in kJ mol^{-1}, standard state; 1 atm and 473 K, experimental error for reaction (3) ±10% and for reaction (1) ±8%

Reaction (3) is an example of the charge transfer reaction. Therefore, it is possible to consider that the value of ΔS° for reaction (3) is nearly zero, and the value of ΔH° is equal to that of ΔG°.[7,8] From reaction (3), the expression for ΔH° is $\Delta G^\circ(3) = \Delta H^\circ(3) = H^\circ{}_{M^+} + H^\circ{}_{(M-O)} - [H^\circ{}_M + H^\circ{}_{(M-O)^+}] = (H^\circ{}_{M^+} - H^\circ{}_M) - [H^\circ{}_{(M-O)^+} - H^\circ{}_{(M-O)}]$ where $(H^\circ{}_{M^+} - H^\circ{}_M)$ and $[H^\circ{}_{(M-O)^+} - H^\circ{}_{(M-O)}]$ are the enthalpy changes for the ionizations of M and $(M - O)$. Therefore, the values of $\Delta H^\circ(3)$ are the differences of the ionization potential between M and $(M - O)$. From the results that the values of $\Delta H^\circ(3)$ for reaction (3) of (Ia—c) are *ca.* −11.7, −12.1, and −17.6 kJ mol^{-1}, the differences of the ionization potential between M and $(M - O)$ are given as *ca.* 0.1, 0.1, and 0.2 eV for (Ia—c), respectively. These differences are in good agreement with those of the ionization potential between picoline *N*-oxides and the corresponding picolines reported as *ca.* 0.3—0.6 eV. A similar relation is shown in the difference of ΔH° between the addition reaction (1a) of (I) and that (1b) of (I) or (1c) of (II) as shown in Table 1. It suggests that picoline *N*-oxides act as ion-trapping reagents to form $(M_2 - O)^+$ species $(CH_3-C_5H_4N-O-NC_5H_4-CH_3)^+$, in a similar manner to Bu^{t}NO. A small discrepancy in reaction (1b) of (Ia) or in (1c) of (IIa) is caused by the formation of hydrogen-bonding species (e).

The following conclusions may be obtained from the results. The addition reaction between Bu^{t}NO and M^+ or $(M - O)^+$ of (I) and that between Bu^{t}NO and M^+ of (II) show that the nitroso-function can be used to study the structure and thermodynamic properties of the organic ions in the gas phase. As well as for Bu^{t}NO, picoline *N*-oxides act as ion-trapping reagents to form the activated complex $(M_2 - O)^+$. The pressure dependence of the mass spectra of picoline *N*-oxides is caused by the effect of the charge transfer reaction between the $(M - O)^+$ species and the neutral molecule through an intermediate $(M_2 - O)^+$ ion.

EXPERIMENTAL

Ion abundances were recorded on a JEOL JMS-D-100 mass spectrometer. At an ionization energy above 20 eV, the experimental data were sometimes scattered, which might be due to the formation of highly excited molecules. Therefore, an electron beam of 11 eV was used for ionization. The chamber temperature of the ion source was controlled in the range 30—300 °C by an ion-source heater, and was measured after for 1—3 h with a thermoelectric thermometer calibrated against a standard.

Bu^{t}NO was synthesized by the method of Stowell,[9] and was further purified by sublimation *in vacuo*. Saturated Bu^{t}NO vapour (4×10^{-4} Torr) at room temperature was diffused from a glass vessel (50 ml) to a gas holder (1 l) through a vacuum cock, and was then introduced into the ion source. The resultant vapour pressure of Bu^{t}NO was 2×10^{-5} Torr.

The preparations of (I) and (II) have been described previously.[1c] They were vapourized in a reservoir (1 l) and were introduced into the ion source through a screw valve. The vapour pressures of (I) and (II) were 2×10^{-6} Torr.

Each value of the equilibrium constant data for van't Hoff plots was the average of 6—12 runs reproducible within 8%.

[1/1934 *Received*, 15*th December*, 1981]

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