Letters to the Editor

Formation of NH_4^+ ions in reaction between urea and nitrous acid

V. P. Gladyshev,* S. V. Kovaleva, and A. V. Korshunov

Institute of Chemical Ecology,
Siberian Branch of International Academy of Creative Endeavors,
Box 238, 634041 Tomsk, Russian Federation.
Fax: +7 (382 2) 41 7155

The interaction of urea and nitrogen oxides produces N_2. This reaction is used in neutralization of nitrogen-containing technological gases and wastes of power, metallurgic, and metal working plants.[1] It is generally accepted[2–4] that urea reacts with nitrous acid according to the equation

$$CO(NH_2)_2 + 2\,HNO_2 \longrightarrow 2\,N_2 + CO_2 + 3\,H_2O. \quad (1)$$

However, in acidic solutions urea may also undergo hydrolysis producing CO_2 and NH_4^+ ions.[4] Available data on the product composition and kinetics of urea reactions with nitrogen oxides and nitrous acid are insufficient for complete description of occurring processes.

We investigated in detail the interaction of HNO_2 with urea in aqueous solutions of HNO_3 containing 0.05—0.2 *M* $CO(NH_2)_2$ and $NaNO_2$ and 0.02—1.0 *M* HNO_3 with magnetic stirring. Time variation of the solution contents was monitored by titrimetry (determination of H^+, HNO_2 and $CO(NH_2)_2$) and ionometry with use of ion-selective electrodes (NH_4^+ and NO_3^-). Gaseous products were identified by IR spectroscopy and with the use of a "Testo-33" automatic gas analyzer.

We found that the reaction between $CO(NH_2)_2$ and HNO_2 within a temperature range of 10—50 °C follows the stoichiometric equation

$$CO(NH_2)_2 + HNO_2 + H^+ \longrightarrow$$
$$\longrightarrow N_2 + NH_4^+ + CO_2 + H_2O. \quad (2)$$

The reaction orders with respect to $CO(NH_2)_2$ and HNO_2 are equal to unity. The effective reaction rate constant k_{eff} grows proportionally to the H^+ ion concentration within the range from 0.01 L mol^{-1} s^{-1} when $[H^+]$ = 0.02 mol L^{-1} to 0.30 L mol^{-1} s^{-1} when $[H^+]$ = 1.0 mol L^{-1} (25.0±0.1 °C). In our opinion, the essential determining factor in the H^+ concentration range under study is the fraction of the protonated form of $CO(NH_2)_2$. Assuming that the reaction involves $H_2NCONH_3^+$, we calculated the rate constant k_0 independent of the H^+ ion concentration with the use of the dissociation constant of the urea protonated form[5]:

$$H_2NCONH_3^+ \rightleftharpoons CO(NH_2)_2 + H^+, \qquad K = 0.66.$$

The concentration of the urea protonated form is determined by the expression

$$[H_2NCONH_3^+] = \frac{[CO(NH_2)_2]_0[H^+]}{K + [H^+]}, \quad (3)$$

where $[H_2NCONH_2]_0 = [CO(NH_2)_2] + [H_2NCONH_3^+]$.

The kinetic equation of the reaction can be presented in the following form

$$v = k_{eff}[CO(NH_2)_2][HNO_2] =$$
$$= k_0\frac{[CO(NH_2)_2]_0[H^+][HNO_2]}{K + [H^+]},$$

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where k_{eff} is the experimentally determined effective rate constant; k_0 is the $[H^+]$ independent rate constant.

$$k_0 = k_{eff}\frac{K+[H^+]}{[H^+]},$$

K is the equilibrium constant of urea. The calculated value of k_0 in the whole investigated $[H^+]$ concentration range amounts to 0.45±0.04 L mol^{-1} s^{-1} (25.0±0.1 °C). Reaction (2) probably proceeds according to a scheme analogous to the mechanism of nitrosation of primary amines[6]:

$$CO(NH_2)_2 \xrightarrow{H^+} H_2NCONH_3^+ \xrightarrow[-H_2O]{HNO_2,\ H^+}$$

$$\longrightarrow [OHN{=}\overset{+}{N}HCONH_3^+] \xrightarrow[-H_2O]{} [N{=}\overset{+}{N}CONH_3^+] \longrightarrow$$

$$\xrightarrow[-N_2,\ H^+]{H_2O} [HOCONH_3^+] \longrightarrow CO_2 + NH_4^+.$$

The fact that NH_4^+ ions have not been detected previously[2,3] may be explained by low acidity of the reaction mixture and, correspondingly, low concentration of protonated urea. Our experiments revealed that an increase in the NH_4^+ and NO_3^- concentrations in the reaction solution *via* introducing $(NH_4)_2SO_4$ and $NaNO_3$ does not lead to a change in the reaction rate. Using the ionometry method we found that the hydrolysis of $CO(NH_2)_2$ yielding NH_4^+ under the conditions of our experiments does not occur. Similar data on the kinetics of interaction of $CO(NH_2)_2$ with HNO_2 were obtained by us in chloric acid solutions (0.02—1.0 *M* $HClO_4$).

Thus, it is necessary to account for the accumulation of ammonium ions in the solutions in the case of employing urea in removing traces of nitrous acid from solutions in analytical practice and during syntheses[4].

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Reaction of diphenyl(trimethylsilyl)phosphine with α-oxo phosphonates

M. M. Kabachnik,* Yu. A. Khomutova, and I. P. Beletskaya

M. V. Lomonosov Moscow State University, Department of Chemistry,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 3618. E-mail: beletska@org.chem.msu.su

We have previously reported[1] that diphenyl(trimethylsilyl)phosphine reacts with carbonyl compounds yielding diphenyl[alkyl(phenyl)trimethylsilyloxymethyl]phosphines. These compounds are of interest because of their potential use as ligands in complexes with transition metals.

In a continuation of these investigations, we studied the addition of diphenyl(trimethylsilyl)phosphine to α-oxo phosphonates. The reaction was completed in 10 min at 10 °C and resulted in the corresponding α-phosphino(α-silyloxy)phosphonates (**2**) in 45—95% yield depending on the structure of the starting oxo phosphonate (Scheme 1, Table 1).

The reaction can be conducted either without a solvent or in anhydrous diethyl ether or hexane. The addition of the solvent has practically no influence on the yield of the target product.

It should be noted that the addition of trimethylsilylphosphine to α-oxo phosphonates easily occurs without a catalyst, as opposed to trimethylsilylcyanide, which adds to carbonyl compounds[2] and oxo phosphonates[3] only in the presence of catalysts, *e.g.*, ZnI_2 or Bu_3SnCN.

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