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SHORT NOTE**K⁺ Ion Formation in Collision of Na⁺ Ions with KCl Vapors**

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In the study on surface ionization of an alkali halide Kawano and Inouye¹⁾ found that the emission of the alkali ions from the halide is suppressed by coexistence of another alkali halide, which involves a heavier alkali ion, on the ionizing metal surface. They have considered that the effect is caused by the fact that a lighter alkali ion M_L^+ combines more strongly with a halide ion X^- than a heavier alkali ion M_H^+ does. If this is the case, one may anticipate a reaction, $M_L^+ + M_HX = M_LX + M_H^+$, to proceed also in the gas phase. A reaction like this in the gas phase does not yet seem to be reported, whereas the reaction $M_1 + M_2X = M_1X + M_2$, where M_1 and M_2 are alkali atoms and X is a halogen atom, was shown to proceed by the complex formation mechanism.^{2), 3)} In this article we describe some results of a preliminary approach to the reaction:

by a crossed beam experiment. Here, $(NaCl)$ expresses a transient molecular system formed just after the reaction. It may lead to a stable $NaCl$ molecule or may dissociate into the

component atoms.

The experimental principle is as follows. The primary ions Na^+ are formed by surface ionization of sodium chloride on a hot rhenium surface. After being extracted from the ion source chamber and being given a selected energy in the range 30–200 eV (in the laboratory system), the Na^+ ion beam crosses a KCl beam effusing from a Knudsen furnace heated to about 800°C. Since the energy of the KCl beam (≤ 0.1 eV) can be ignored compared to the Na^+ beam energy, one may assume that KCl molecules in the reaction volume are at rest in the laboratory system. Potassium ions, if produced, are extracted out of the reaction volume by an electrostatic field across the volume. The Na^+ and K^+ ions are monitored by a conventional mass spectrometer of magnetic deflection type. The peak of the K^+ ions in the mass spectra should be displaced from the normal location, i. e., that of the K^+ ions formed on the ionizing surface, towards the low mass side by an amount ΔV_p corresponding to the energy defect $e(\Delta V_a - \Delta V_i)$, ΔV_a being the potential difference between the ionizing surface and

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the passage of the KCl beam, and ΔV_i being an initial kinetic energy that the ions possess at the moment of production. Thus, the initial kinetic energy can be determined by scanning acceleration voltage with keeping the magnetic field constant. Magnitude of the initial kinetic energy of the K^+ ions thus formed gives a clue to the reaction mechanism. Our observation, however, is restricted to scattering through c. m. angles in the vicinity of 0° and 180° , because the present apparatus can detect only those of the scattered Na^+ and product K^+ ions whose momenta and the force of the ion acceleration field provide resultant vectors lying within 3° (lab angle) with respect to the primary Na^+ beam axis.

Fig. 1. Mass spectra showing an extra K^+ peak appearing in collisions of Na^+ ions with KCl vapors. The spectra have been displayed on an XY-recorder by voltage scanning.

An example of the mass spectra is shown in Fig. 1, which clearly shows an extra K^+ peak in the neighborhood of the K^+ peak appearing at the normal location owing to potassium contained as an impurity in sodium chloride. The Na^+ peak is, however, attended by no subsidiary peak nor shows peak broadening. The extra K^+ peak disappears when the Na^+ ions or KCl beams are shut off. The normal K^+ peak was used as the reference for determining the peak shift ΔV_p . In Fig. 2 the peak shift is plotted against the potential differ-

ence ΔV_a . The result gives a straight line passing through the origin of the coordinates and having the slope 45° . This means that the K^+ ions produced in the reaction (1) have no appreciable initial kinetic energy greater than thermal energies. Lack of the resolution of the mass spectrometer made separation of the two K^+ peaks difficult below 30 eV for ΔV_a .

If the K^+ ions are produced by dissociation of the collision complex ($NaKCl^+$) formed in the reaction, the K^+ ions should have a certain initial kinetic energy depending on the kinetic energy $T_0 (= e\Delta V_a)$ of the Na^+ ions and an internal energy change ΔE of the collision system. An approximate value of the initial kinetic energy estimated by collision dynamics amounts to $0.1 T_0$ for the process.⁴⁾ If the K^+ ions are formed *via* excitation or dissociative ionization of the target molecule by Na^+ impact, a subsidiary Na^+ peak or peak broadening due to an energy loss in the collision should appear about the main Na^+ peak. The energy loss is given approximately by $0.7 T_0 + 0.6 \Delta E$, where ΔE is an internal energy gain of the collision system and has the value about 9 eV,⁵⁾ if it is assumed as the appearance potential of K^+ from KCl. The initial kinetic energy of the K^+ ions formed in this case is given approximately by $0.7 T_0 - 0.4 \Delta E$. The experimental results that the K^+ ions have no appreciable initial kinetic energy and that no subsidiary Na^+ peak has been found in the spectra will suggest that the above two processes are not responsible for the reaction.

One of the possible processes conceivable as the cause of the phenomena is an impulsive collision of the Na^+ ion with the Cl^- ion of the target KCl molecule.⁶⁾ If the reaction proceeds by a process in which a Na^+ ion interacts only with the Cl^- ion of a KCl molecule with no momentum transfer to the partner K^+ ion, then the liberated K^+ does not possess an initial

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Fig. 2. Plot of the peak shift ΔV_p against the potential difference ΔV_a between the ionizing surface and the passage of KCl beams.

kinetic energy greater than that into which a part of the heat of reaction is transformed. The Na⁺ ions are not attended by any subsidiary peak, since the resultant (NaCl) molecules or the atoms produced by the dissociation of (NaCl) in virtue of its large internal energy have no net charge. Explanation of the experimental results by the last process, therefore, seems more attractive than by either of the first two processes. This presumption may appear at first sight to be inconsistent with the results on the atom transfer reaction mentioned early, but it is by no means strange since the beam energy employed in this work is much higher than that used in the atom transfer reaction experiments. Lowering the kinetic energy of the primary Na⁺ ions below 30 eV might cause transition of the process from one described above to "complex formation",^{7), 8)} or to "modified stripping".^{9), 10)} As stated early, the information obtained from this experiment

is confined only to that on small angle scattering, and, therefore, the discussion given just above is not conclusive. An alternative process is possible as the major process governing the Na⁺ + KCl reaction. Establishment of the overall reaction mechanism requires further investigation to determine the differential cross sections of the reactive scattering.

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