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Reaction of CO− 3, NO− 3, and CO− 4 with atomic hydrogen

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LETTERS TO THE EDITOR

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NOTES

Reaction of CO_3^-, NO_3^-, and CO_4^- with atomic hydrogen

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Studies carried out in this laboratory over the past several years have investigated many negative ion reactions with atomic hydrogen.[1-7] Atomic hydrogen reacts readily with a wide variety of negative ions. Some of these reactions are of significance in aeronomy,[5] astrophysics,[1,8] radiation chemistry,[9] and combustion.[10] In the present measurements the reaction rates of atomic hydrogen with CO_4^-, CO_3^-, NO_3^-, and SO_4^- have been investigated at 296 °K. The reactions of CO_4^-, CO_3^-, and NO_3^- are of particular importance since CO_3^-, CO_4^-, and NO_3^- are important in the negative ion chemistry of air and airlike mixtures.

The experimental details of the present measurements were discussed in detail in Ref. 7. Atomic hydrogen was produced by thermal dissociation of H_2 on a hot tungsten filament.[11] The concentration of atomic hydrogen in the reaction region was determined from the decline of a Cl^- monitor ion signal. Either SF_6 or CF_3I was added before the reaction region to remove electrons freed by detachment reactions. All of the present measurements were made in an O_2 buffer. The estimated accuracy of the rate constant reported here is ±40%. The measured rate constants are for the reaction into all channels. The determination of the contribution of individual channels where several product ions were observed was not attempted quantitatively since the product ions usually reacted rapidly with atomic hydrogen.

The results obtained in the present measurements are listed in Table I. The reaction rate constants listed are referenced against the rate constant for the reaction between Cl^- and H, $k_1 = 9.6 \pm 0.9 \times 10^{-10}$ cm³/sec.[7] The rate constants for the reaction of H with O_2^-, O_3^-, and NO_2^- which have been measured previously were redetermined as a check. The agreement between the present results and previous measurements is excellent.

CO_4^- reacts with H to give principally CO_3^-. OH^- was also observed to increase. However, OH^- was also produced by the reaction of CO_3^- with H (Reaction 6) and NO_2^- with H (Reaction 3). CO_3^- reacts with H giving OH^- as the only observed product.

There are two isomeric forms of NO_3^- which exhibit considerably different reactivities.[12] The less stable form NO_3^{-*} was produced in the present measurement by the switching reaction between $O_2^- \cdot O_2$ and NO. This NO_3^{-*} was rapidly attacked by atomic hydrogen producing NO_2^-, a mechanism analogous to Reaction 5 where CO_3^- was produced from CO_4^-. OH^- was also observed to increase although this OH^- was produced at least in part by Reaction 3.

The stable form of NO_3^- was formed by the reaction of NO_2^- with O_3 or O_3^- with NO_2. In this case, the NO_3^- so formed was not found to react with H, placing an upper limit on $k_8 < 5 \times 10^{-11}$ cm³/sec.

Finally, SO_4^{-*} was found to react with H. As in the case of NO_3^-, two isomeric forms of this ion are known to exist which exhibit considerably different reactivities.[12] In this work only the reaction with the less stable form SO_4^{-*} was investigated. SO_4^{-*} was produced by the association of SO_2^- with O_2 in the oxygen buffer and by the switching reaction of SO_2 with $O_2^- \cdot O_2$. SO_2^- and a small quantity of an ion at mass 33, which we believe to be

TABLE I. Reaction rate constants of various negative ions with atomic hydrogen.

Reaction	Rate constant (10^{-10} cm³/sec)	Reference
1. $Cl^- + H \rightarrow HCl + e$	9.6	7
2. $O_2^- + H \rightarrow HO_2 + e$	14	This work
	12	7
$\rightarrow H^- + O_2$	15	6
3. $NO_2^- + H \rightarrow OH^- + NO$	3.7	This work
	4	6
	3	5
4. $O_3^- + H \rightarrow OH^- + O_2$	8.4	This work
	8.4	6
5. $CO_4^- + H \rightarrow CO_3^- + OH$ $\rightarrow OH^- + CO_3$	2.2	This work
6. $CO_3^- + H \rightarrow OH^- + CO_2$	1.7	This work
7. $NO_3^{-*} + H \rightarrow NO_2^- + OH$ $\rightarrow OH^- + NO_2$	7.2	This work
8. $NO_3^- + H \rightarrow$ products	< 0.5	This work
9. $SO_4^{-*} + H \rightarrow SO_2^- + HO_2$ $\rightarrow HO_2^- + SO_2$	1.6	This work

O_2H^- (as opposed to SH^-), was observed to be produced in the reaction.

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About the collision induced Raman spectrum of gaseous argon*

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The Raman spectrum of gaseous argon at room temperature and at pressures of a few atmospheres consists of two nearly identical wings of completely unpolarized radiation and extends to shifts of about 50 wavenumbers.[1-4] Probably ~90% of the intensity found in the wings is a result of collision-induced light scattering (C.I.S.) of free pairs of atoms in an encounter.[5] Theoretical studies of C.I.S. based on classical path treatment have appeared,[1,6,7] but the complexity is considerable and various simplifying assumptions are usually made for tractability, as well as for generality of conclusions. As a consequence, although there is a good general consistency of the gross (or asymptotic) features, in the case of argon, theory is at present not in complete agreement with the experiments. For example, one striking detail of our observation[3] (shown in Fig. 1), a maximum at ± 8.3 cm^{-1} wavenumbers (which shifts with temperature), remained unexplained.

In an attempt to understand the nature of this maximum, we have studied C.I.S. in the classical path approximation again, emphasizing an accurate accounting for the low frequency components from 1 to 30 cm^{-1}. Following Gersten (Formula 2′ of Ref. 7), we obtain the spectral intensities as the sum of the squares of the Fourier transforms $\int e^{i(\omega-\omega_0)t}\gamma(r)e^{i\lambda\varphi}\,dt$, with $\lambda = 0, \pm 2$. Here $(\omega-\omega_0)$ designates the frequency shifts and $\gamma(r) = \alpha_{\parallel} - \alpha_{\perp}$ the induced anisotropy of the polarizability tensor $\tilde{\alpha}$. With the help of a digital computer, and with an assumed MSV III interaction potential,[8] the classical path coordinates of separation r and polar angle φ are computed as function of time t, for fixed values of the initial relative speed v and impact parameter b. We then integrate over b and finally average over all speeds v, accounting for their Maxwellian distribution. With a suitable expression for the anisotropy γ, the theoretical spectra shown in Fig. 1 are obtained.

The simplest choice for the induced anisotropy $\gamma(r)$ is an inverse third power of the separation $\gamma(r) \sim (1/r)^3$ ("point dipole approximation"). From Hartree–Fock type calculations[9] of the polarizability tensor of argon we obtain a more accurate expression $\gamma(r) = 0.3544\,(x - 0.55x^2 + .025x^3)$ Å^3, with $x = (3.405\ \text{Å}/r)^3$, which is valid for $r \gtrsim 3$ Å. Since the cubic term is of little significance we used $\gamma(r) = x - 0.55x^2$ (Labeled "Hartree–Fock" in Fig. 1. The numerical factor of 0.3544 Å^3 is suppressed as absolute intensity measurements have not been made.) We have also tried other models[10] of γ containing higher inverse powers of r. Under no circumstances, however, was the shape of the computed spectra modified enough by such choices to reproduce (or even

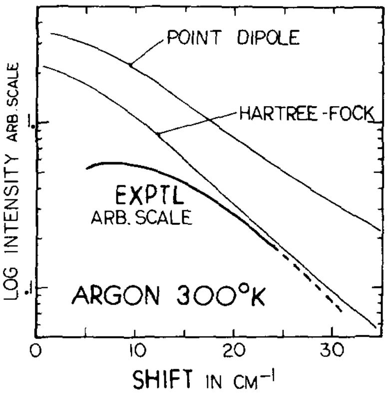

FIG. 1. Theoretical collision-induced Raman spectrum in argon (300 °K) in the classical trajectory approximation. Two different models of the anisotropy of the polarizability tensor were used (see the text for details). For comparison, the experimental spectrum of Ref. 3 is also given.