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ENERGY AND MASS DEPENDENCE OF THE PRODUCT YIELDS IN THE REACTION OF METHANOL WITH ACCELERATED INERT GAS IONS

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Ion impact reaction of methanol was studied with accelerated inert gas ions with initial energy from 2-6 kV. It is shown that the yields are linear vs. $\ln E_i$, and the ratio of the average logarithmic energy loss to the reaction probability (α/p_j) was determined. The dependence of α on mass of the projectile ion is discussed.

In the previous papers[1)] we reported a technique to study the ion impact reaction and some results on the reaction of methanol. In the present paper we report the energy dependence of the product yields (Y_{H_2}, Y_{CO} and Y_{CH_4}) with Ne, Ar, Kr, Xe and N_2 ions. The main features of the apparatus and procedures were reported in the previous papers, and their some modifications for improvement will be reported elsewhere.

In Fig. 1 (a, b and c), the plots of the product yields (Y_{H_2}, Y_{CO} and Y_{CH_4}, in unit of molecule per ion) vs. $\ln E_i$ are presented, showing a good linear relationship for each case. The slopes of the plots are determined by the least square method, and their reciprocal values are shown in Table 1.

Although the detailed reaction mechanism to yield these reaction products is not established yet, the interpretation of the results is attempted on the basis of the hot atom slowing down theory. We assumed that the product yield Y_j is given in terms of integrated collision numbers according to the Miller-Dodson formula[2)]:

$$Y_j=\int_{E_2}^{E_1} p_j(E)n(E)dE, \qquad (1)$$

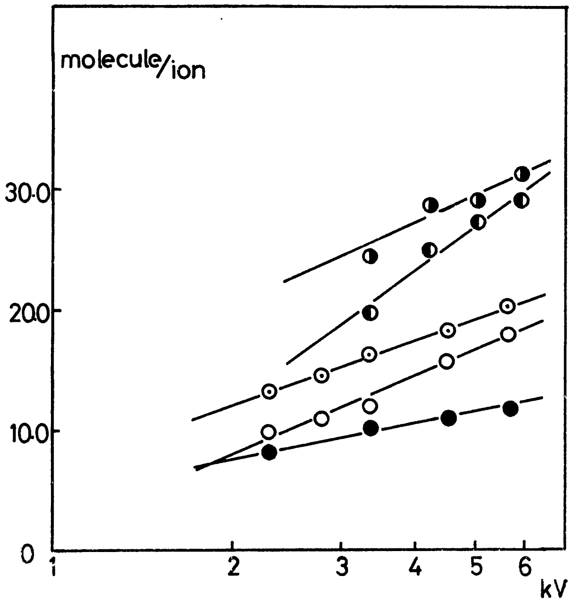
where n(E) is the collision density function (numbers of collision per unit energy at energy E). In order to obtain the exact form of n(E), it is necessary to solve an integral equation, which includes the scattering function of a collision, K(E,E') as its kernel. $p_j(E)$ is the reaction probability to give the j-th product by a collision at E, and E_1 and E_2 are the upper and lower limits of nonzero p_j, respectively. In the case of isotropic scattering, it is well known that the asymptotic form of n(E) is given in the following formula:

$$n(E)=(\alpha E)^{-1}, \qquad (2)$$

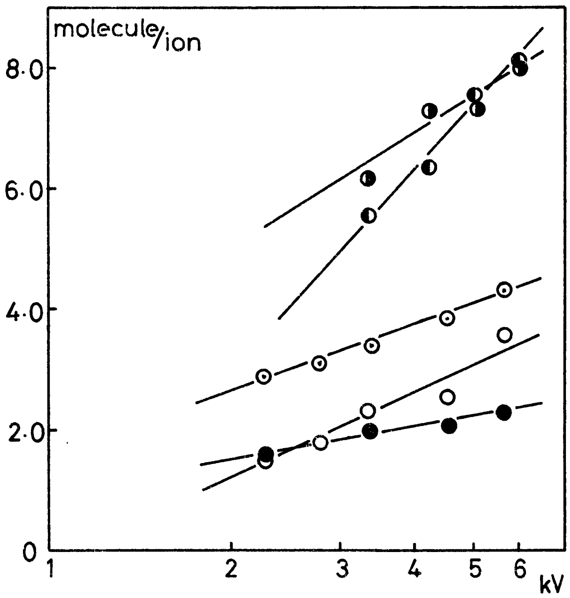
where α is an energy independent constant. It has been shown that α is equal to the average logarithmic energy loss defined as:

$$\alpha=\int_{\beta E}^{E} \ln(E/E')K(E,E')dE', \qquad (3)$$

and for isotropic scattering it is a function of β only as follows,

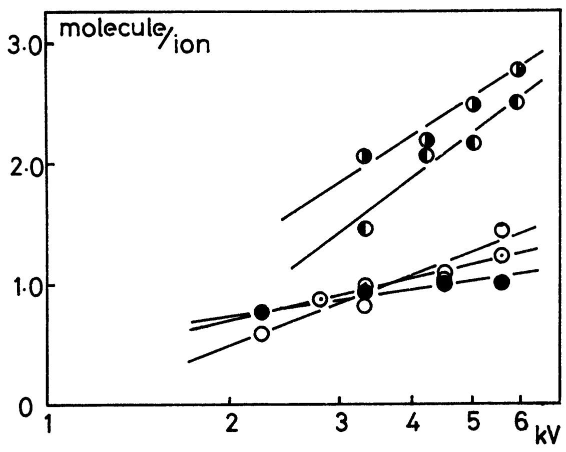


(a) H_2



(b) CO

Fig. 1. Plot of the product yields vs. $\ln E_i$ for Ne, Ar, Kr, Xe and N_2 ions. o; Ne, ●; Ar, ◑; Kr, ◐; Xe, ⊙; N_2.



(c) CH_4

Table 1. The average logarithmic energy loss and the reaction probability determined from the slopes in Fig. 1.

Inert gas ions	Product	α/p_j	Energy loss parameter β	α_{iso}	α_{anis}	p_j
Ne	H_2	0.11				2.00
(20.179)	CO	0.49	0.0513	0.84	0.22	0.45
	CH_4	1.20				0.18
Ar	H_2	0.26				0.92
(39.948)	CO	1.31	0.0122	0.95	0.24	0.18
	CH_4	3.41				0.07
Kr	H_2	0.090				1.78
(83.80)	CO	0.32	0.2001	0.60	0.16	0.50
	CH_4	0.81				0.20
Xe	H_2	0.061				1.97
(131.30)	CO	0.21	0.3698	0.42	0.12	0.57
	CH_4	0.57				0.21
N_2	H_2	0.13				1.92
(28.016)	CO	0.60	0.0044	0.98	0.25	0.42
	CH_4	2.05				0.12

$$\alpha=1+\beta\ln\beta/(1-\beta), \qquad (4)$$

where $\beta=((m_1-m_2)/(m_1+m_2))^2$, m_1 and m_2 ; mass of a collision pair. However, it has been pointed out that the isotropic scattering model is far from the realistic one for the case of hot atom impact. Porter and Kunt[3] proposed two types of trial functions for K(E,E'), both of which are weighted for the forward scattering. In the fifth and sixth columns of Table 1, we tabulated α for isotropic scattering (α_{iso}) and α for anisotropic one (α_{anis}) calculated using Porter's model C, respectively.

To a rough approximation, if we could assume p_j is independent or very insensitive to ion energy E, we would obtain the integral reaction yield Y_j in the following way:

$$Y_j=(p_j/\alpha)\ln(E_i/E_f), \qquad (5)$$

where E_i and E_f are the initial and final values of ion energy, respectively, although in the present experiment the meaning of E_i and E_f is rather ambiguous. Here we assumed that E_i is the energy of the projectile ion set up by the experiment and that $\ln E_f$ is small enough compared with $\ln E_i$. Our experimental finding that Y_js are well proportioal to $\ln E_i$ may be considered to justify these assumptions. Combining the values of α/p_j determined by the present experiment with those of calculated α_{anis}, we calculated p_j as shown in the seventh column of Table 1. It is interesting that p_j for each product are nearly identical irrespective of the ionic species, apart from the case of Ar. This may indicate that in the ion impact of relatively high energy the product yields are only dependent on the integrated collision numbers (in another words, $\ln(E_i/E_f)/\alpha$) and that the chemical specifity of the projectile ion to methanol is lost, as far as Ne, Kr, Xe and N_2 ions are concerned in the present experiment. Although p_j must be less than unity in the general case, $p_{H_2}\sim 2$ may be not unreasonable, if we assume that more than one molecule of H_2 can be produced by a single collision. If we take the values of α_{iso} instead of α_{anis} to calculate p_j, we will obtain p_j about four times smaller than those shown in Table 1, since the ratios $\alpha_{iso}/\alpha_{anis}$ are about four, irrespective of the ionic species. Any definite explanation for the smaller values of p_j for Ar is not available at present.

Finally we have to point out that the interpretation presented above is still of the very tentative nature. The detailed mechanism to yield the reaction products is quite uncertain, and probably several competing reaction channels are involved. It must be elucidated whether they are produced through a unimolecular decomposition or some successive processes, although the similar question may be raised to the studies of photochemical or radiation chemical decomposition of methanol. Another point to be considered is whether all products are produced in the vapor phase of methanol, since there is left the possibility that some fraction of the products is due to the ion impact reaction with solid methanol recovered in the exit part of the reaction tube. We will report further investigations to elucidate these points in the succeeding paper.

References

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