difluoroacetate. In general, it appears that an increase in the extent of fluorination of an organic compound results in an increase in thermal expansion coefficient.

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Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. IV. Effect of Noble Gases

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The rate of the reaction $N_2O_5 + NO \rightarrow 3NO_2$ has been shown by Smith and Daniels[1] and by Mills and Johnston[2] to be that of an elementary unimolecular reaction. At around 0.1 mm. pressure in a 22-liter flask, the reaction is homogeneous and definitely within the second-order region.[3] The low-concentration second-order rate constants of a series of gases have been reported.[4]

Using the 22-liter bulb, and the same method of interpreting the data as was used previously,[3,4] we have determined the low-concentration second-order rate constants of the noble gases and carbon tetrachloride. Reactant pressures were each about 0.08 mm., and foreign gas pressures ranged from 3 to 0.02 mm. Experimental results are given in Table I.

TABLE I

EXPERIMENTAL RESULTS

M gas	No. of points	Intercept, sec.$^{-1}$	Low concn. second-order rate constant, cc. mole^{-1} sec.$^{-1}$ × 10^5 Value	Standard error	Ratio to pure N_2O_5
He	27	0.0132	2.80	0.26	0.124
Ne	17	.0129	2.02	.32	.090
Kr	26	.0119	3.57	.23	.159
Xe	11	.0134	3.30	.95	.147
CCl_4	30	.0130	12.4	1.3	.551

As shown previously, the activating efficiency function of the state i above the critical energy, a_{Mi}, can be written as $a_{Mi} = b_{Mi}P_i$, that is, the relative activating efficiency is also the relative deactivating efficiency. The function b_{Mi} is further factored, $b_{Mi} = b_M f_{Mi}$, where b_M is the kinetic collision constant

$$b_M = N_0 \left[8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]^{1/2}\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \quad (1)$$

where N_0 is Avogadro's number; σ_1 and σ_2, the collision diameters of the colliding particles; M_1 and M_2, the molecular weights of the colliding particles; and R and T have their usual meaning. The function f_{Mi} is the efficiency factor for deactivation which in general may be a function of each state i and a different function for each foreign gas M.

If the collision constant can be calculated by 1, then the relative efficiencies with b_M factored out give the ratios $\overline{(f_M)}/\overline{(f_1)}$, where 1 stands for nitrogen pentoxide, and the bar indicates an average with respect to P_i over the excited states. If deactivation occurred at every collision or if f_{Mi} depended on the quantum states i of the reactant molecule only but not on the identity of the foreign gas M, this ratio would be unity every time. It is not. (See Table II. This table includes data calculated from reference 4.)

TABLE II

EFFICIENCY AND RELATIVE EFFICIENCY

M gas	Mol. wt.	Collision diameter, Å.	Low concn. rate const./kinetic collision const., $\overline{(f_M)} \times 10^{10}$	$\overline{(f_M)}/\overline{(f_1)}$
He	4	2.18[a]	6.02	0.0650
Ne	20	2.59[a]	7.95	.0855
A	40	3.64[a]	14.3	.154
Kr	83.8	4.16[a]	19.3	.208
Xe	131.3	4.85[a]	17.5	.189
N_2	28	3.75[a]	21.2	.228
NO	30	3.75	27.9	.300
CO_2	44	4.59[a]	35.9	.387
CCl_4	154	5.46	62.5	.673
SF_6	146	4.52	41.2	.443
N_2O_5	108	6.00	93.0	1.000

[a] From E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 149.

Furthermore, it is impossible to adjust the collision diameters of either nitrogen pentoxide or of the various M gases to obtain ratios $\overline{(f_M)}/\overline{(f_1)}$ that are equal to unity. For the molecular weights are accurately known, and the ratio, $(2\sigma_{N_2O_5}/\sigma_{N_2O_5} + \sigma_M)^2$, can never be greater than 4, which is not sufficiently large to account for the observed relative efficiencies of the noble gases and nitrogen. Thus, the efficiency function f_{Mi} does differ markedly from one gas to another. (These results do not answer the question as to whether or how the efficiency function varies over the states i of the reactant molecule.)

Relative efficiency increases slowly with molecular weight through at least krypton for the noble gases. It increases at constant molecular weight as one goes from noble gases to diatomic or polyatomic gases, and nitrogen pentoxide is much more efficient than anything else we have yet used. A study of the relative efficiencies of diatomic and polar gases is now in progress.

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