ISOTOPIC EXCHANGE REACTIONS OF DIFLUORAMINE WITH DEUTERIUM OXIDE AND TRIFLUOROACETIC ACID

Warren E. Becker and Fred J. Impastato
Ethyl Corporation, Baton Rouge, La.

The isotopic exchange of hydrogen between HNF_2 and D_2O was followed by NMR using deuterated tetrahydrofuran-d8 as solvent. The growth of the H_2O peak was followed by NMR and the fraction of exchange F at time t was calculated by dividing the area of the H_2O peak at time t by the area at time t ∞. The half-life of exchange $t\frac{1}{2}$ was obtained from the plot of log (1-F) vs. t which, of course, is linear. The rate of exchange R was then calculated from the equation

$$R = \frac{2[D_2O][HNF_2]}{2[D_2O] + [HNF_2]} \cdot \frac{0.693}{t\frac{1}{2}} \qquad (1)$$

The exchange of hydrogen between HNF_2 and D_2O is first order with respect to HNF_2 and zero order with respect to water as shown in Table I. A reasonable mechanism is

$HNF_2 = H^+ + NF_2^-$ Slow

$H^+ + D_2O = D^+ + H_2O$ Fast

$D^+ + NF_2^- = DNF_2$ Fast

where the rate-determining step is the ionization of HNF_2.

The exchange was followed at several temperatures by using a temperature-controlled probe which regulated the temperature to $\pm$ 1°C. The activation energy of 4.5 kcal/mole was calculated from the Arrhenius equation. The plot of log K vs. 1/T is shown in Figure 1.

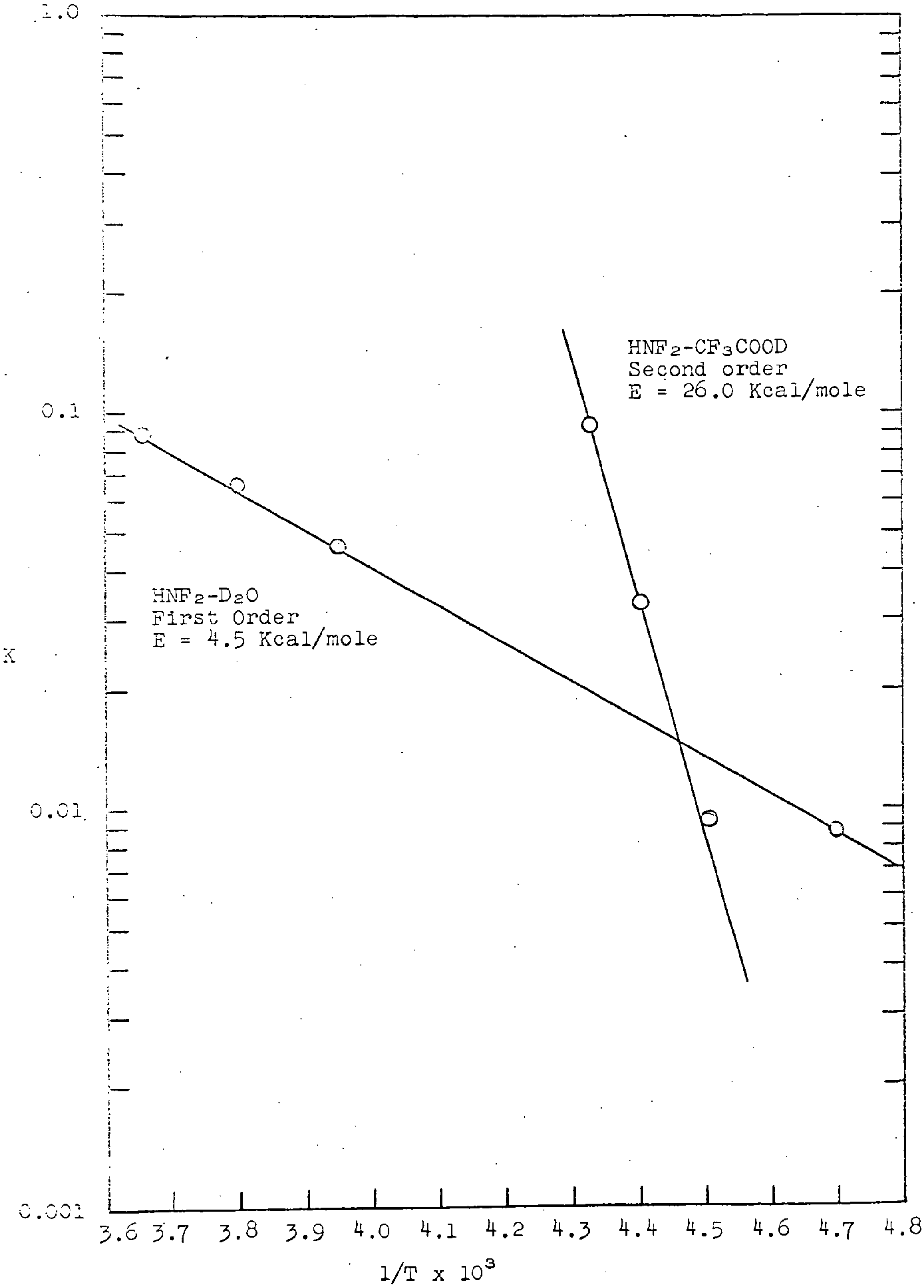
The fact that the exchange is acid catalyzed induced us to investigate the exchange of hydrogen between HNF_2 and

Table I

Summary of HNF_2-D_2O Exchange Runs

Conc. moles $l.^{-1}$ $[D_2O]$	$[HNF_2]$	$t_{1/2}$ (min)	R (moles l^{-1} min^{-1})		K (min^{-1})	t°C
1.27	1.28	9.2	0.064		0.050	-20
1.40	0.69	11.3	0.034		0.049	-20
0.64	1.18	13.4	0.060		0.051	-20
1.91	1.16	9.8	0.063		0.054	-20
1.38	2.08	10.3	0.080		0.038	-20
1.31	1.87	10.3	0.073		0.039	-20
1.04	0.28	14.1	0.012		0.043	-20
				Avg.	0.046	
1.97	1.02	11.8	0.048		0.047	-10
1.97	2.02	6.2	0.150		0.075	-10
2.80	2.03	6.7	0.154		0.076	-10
				Avg.	0.066	
2.82	1.38	5.3	0.144		0.105	0
1.36	1.52	6.3	0.107		0.070	0
				Avg.	0.088	

Figure 1. Temperature Dependence of Rate Constants



CF_3COOD. This exchange was also studied in deuterated tetrahydrofuran-d8 at several temperatures. The results are summarized in Table II.

The mechanism found for the exchange of hydrogen between HNF_2 and D_2O (the ionization of HNF_2) will also lead to exchange of hydrogen between HNF_2 and CF_3COOD. Therefore, we must subtract the contribution of this first order mechanism from the total rate of exchange. The rate of exchange R, then, is the sum of two rates.

$$R_{total} = K_1[HNF_2] + K_2[HNF_2][CF_3COOD]$$

At -60° only the first order path is observed and the first order rate constant falls on the same line in the Arrhenius plot as the points obtained for the HNF_2-D_2O exchange. This is shown in Figure 1.

At -51° both paths proceed at about the same rate while at higher temperatures the second order path proceeds faster. The activation energy for the second order path is 26.0 kcal/mole. The Arrhenius plot for this path is shown in Figure 1 which also shows that the plots for the two paths intercept at about -50°C.

There are two possible mechanisms for the second order path as shown below. The first is the protonation of HNF_2

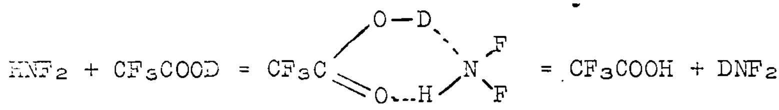
$HNF_2 + CF_3COOD = HDNF_2^+ + CF_3COO^-$	Slow
$HDNF_2^+ = DNF_2 + H^+$	Fast
$H^+ + CF_3COO^- = CF_3COOH$	Fast

Table II

Summary of HNF_2-CF_3COOD Exchange Runs

Conc. moles $l.^{-1}$ [HNF_2]	Conc. moles $l.^{-1}$ [CF_3COOD]	$t_{1/2}$ (min)	R(moles l^{-1} min^{-1})	R from 1st Order Path	R from 2nd Order Path	2nd Order K (l $mole^{-1}$ min^{-1})	1st Order K (min^{-1})	t°C
1.53	0.95	30.5	0.0133				0.0087	-60
1.56	1.98	46.0	0.0131				0.0084	-60
1.50	1.50	36.4	0.0143				0.0095	-60
1.47	0.75	30.1	0.0114				0.0078	-60
0.81	1.45	39.3	0.0092				0.0113	-60
0.72	1.52	74.4	0.0046				0.0063	-60
						Avg.	0.0087	
1.56	1.84	1.86	0.315	0.031	0.284	0.099		-42
0.78	1.76	2.75	0.136	0.015	0.121	0.088		-42
0.83	0.47	3.98	0.052	0.016	0.036	0.092		-42
					Avg.	0.093		
1.02	2.00	7.2	0.065	0.017	0.048	0.024		-46
0.96	0.98	8.5	0.040	0.016	0.024	0.026		-46
2.05	1.01	4.4	0.107	0.034	0.073	0.035		-46
0.96	1.98	4.3	0.104	0.016	0.088	0.046		-46
					Avg.	0.033		
1.43	0.75	18.1	0.0188	0.0190	-			-51
1.52	1.50	12.6	0.0415	0.0202	0.0213	0.0094		-51
0.83	0.75	27.3	0.0100	0.0110	-			-51

while the second involves a 1:1 complex



The relative merits of these mechanisms will be discussed.