

**934.** *Reactions of Difluoroamino-radicals. Part I. Hydrogen Abstraction from Acetone and the Strength of the C-H Bond in Acetone*

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The reaction  $\text{NF}_2\cdot + \text{CH}_3\text{COCH}_3 = \text{NF}_2\text{H} + \cdot\text{CH}_2\text{COCH}_3$  has been studied by allowing mixtures of acetone and tetrafluorohydrazine to react in a static system and following the consumption of acetone. The rate constant is given by  $(178\text{--}280^\circ) \log k_2(\text{mole}^{-1} \text{ c.c. sec.}^{-1}) = 10.71 \pm 0.048 - (19,560 \pm 110/2.3RT)$ . The bond dissociation energy  $D(\text{CH}_3\text{COCH}_2\text{-H})$  is deduced to be  $92.1 \pm 1 \text{ kcal. mole}^{-1}$ .

It has recently been shown<sup>1</sup> that reliable information on bond dissociation energies in hydrocarbons can be obtained by allowing them to react with difluoroamino-radicals generated from tetrafluorohydrazine, and by following the reaction by the uptake of hydrocarbon. The method has been applied here to the reactions of these radicals with acetone, to obtain information on the bond strength  $D(\text{CH}_3\text{COCH}_2\text{-H})$ .

EXPERIMENTAL

*Materials.*—Tetrafluorohydrazine was a product of Air Products Inc., U.S.A. Acetone was B.D.H. AnalaR grade. Both were bulb-to-bulb distilled and thoroughly degassed before use.

*Apparatus and Procedure.*—Reactions were carried out in a Pyrex reaction vessel (94.6 c.c.) fitted with a neoprene-diaphragm greaseless stopcock and heated by a vapour jacket. Temperatures were measured by a thermometer placed in the vapour, near the return-tube of a water condenser attached to the vapour jacket. Acetone was admitted to the reaction vessel by expanding a measured pressure from a gas burette, also fitted with a greaseless stopcock, via a constant volume of connecting tubing. A large excess of the hydrazine was then added

<sup>1</sup> J. Grzechowiak, J. A. Kerr, and A. F. Trotman-Dickenson, *Chem. Comm.*, 1965, 109.

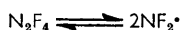
to the cell and the pressure noted on a glass-spiral manometer. At the end of a run, the products and unchanged starting materials were condensed into a Le Roy still and the difluoroamine and tetrafluorohydrazine pumped off at  $-140^\circ$ . The remainder of the products and unchanged acetone were then condensed into the injection loop of a gas-chromatographic analysis system.

*Analysis.*—Acetone was analysed on a 10-ft. column packed with 60–80 mesh Celite impregnated with 15% by weight of dinonyl phthalate. The signal from a hot-wire detector was fed into a 1 mv recorder; the carrier gas was nitrogen. Calibrations were made by passing known amounts of acetone vapour, measured in the gas burette, through the column; a calibration of the reaction vessel was also necessary at each reaction temperature. Acetone, admitted to the reaction vessel as described above, was withdrawn for analysis without reaction taking place, and a calibration plot of gas-burette pressure against peak area on the chromatogram was made. Hence, from this plot and the previous calibration, the amount of acetone admitted to the reaction vessel could be determined from the pressure measured in the gas burette.

Greaseless stopcocks or metal valves were used throughout the reaction and analytical sections of the apparatus.

### RESULTS AND DISCUSSION

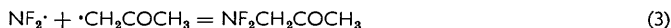
The conditions and analytical results of runs carried out at 178, 211, 237, and  $280^\circ$  are shown in the Table. At these temperatures and at the relatively low pressures of our experiments, tetrafluorohydrazine is mainly dissociated into difluoroamino-radicals,



The concentrations of  $\text{NF}_2\cdot$  radicals listed in the Table were calculated from the pressure of tetrafluorohydrazine put into the reaction vessel and the equilibrium constant ( $K_1$ ) determined by Johnson and Colburn.<sup>2</sup> In view of the results obtained with alkanes,<sup>1</sup> where wide variations in the concentrations of reactants indicated that the hydrocarbon is consumed by a simple hydrogen-abstraction reaction of the  $\text{NF}_2\cdot$  radicals, it seems likely that a similar reaction is involved here *i.e.*



which may be followed by



The rate constants ( $k_2$ ), calculated as described below, are consistent with this mechanism. Other reactions of the acetyl radicals can be neglected owing to the high concentrations of  $\text{NF}_2\cdot$  radicals. No attempt was made to determine the product of reaction (3), since previous experiments with alkanes had shown that difluoroamines are unstable at these temperatures.

The reactions of difluoroamino-radicals with acetone

Temp.	Run time (sec.)	[Me <sub>2</sub> CO] Initial (10 <sup>8</sup> mole c.c. <sup>-1</sup> )	[Me <sub>2</sub> CO] Final (10 <sup>8</sup> mole c.c. <sup>-1</sup> )	N <sub>2</sub> F <sub>4</sub> * (cm.)	[NF <sub>2</sub> ] (10 <sup>7</sup> mole c.c. <sup>-1</sup> )	k <sub>2</sub> (mole <sup>-1</sup> c.c. sec. <sup>-1</sup> )
178°	9000	7.89	6.85	3.92	10.5	15.6
178	39,600	6.43	3.81	2.75	7.77	17.5
178	18,000	6.72	4.99	4.10	10.8	15.8
178	54,000	6.29	3.29	2.58	7.27	17.3
211	15,300	6.97	1.66	3.90	11.5	80.8
211	8100	6.48	3.24	3.84	11.3	78.4
211	19,800	6.63	2.40	2.35	7.26	75.9
211	7800	7.21	4.76	2.18	6.75	82.5
237	1800	6.95	5.20	2.48	7.65	218
237	900	6.50	5.02	4.52	13.8	214
237	3600	6.45	3.80	2.47	7.64	200
237	1800	6.88	4.49	4.25	12.9	192
280	600	6.58	3.87	3.22	9.12	1000
280	600	5.89	3.67	3.00	8.48	955
280	300	6.13	4.15	5.12	14.5	917
280	300	6.09	4.15	5.12	14.5	906

\* Initial pressure admitted to reaction vessel.

<sup>2</sup> F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.

Rate constants ( $k_2$ ) for reaction (2) were calculated from the equation:

$$k_2 t = \frac{1}{2} [a - (b/2)]^{-1} \ln \left( \frac{(a-x)/a}{(b-2x)/b} \right)$$

where  $t$  = run time,  $a$  = initial concentration of acetone,  $b$  = initial concentration of  $\text{NF}_2\cdot$  radicals and  $x$  = concentration of acetone consumed. As seen from the Table the values of  $k_2$  at a given temperature were consistent and independent of acetone or hydrazine concentrations and extent of reaction. A least-mean-squares calculation of the rate constants gave  $\log k_2$  (mole<sup>-1</sup> c.c. sec.<sup>-1</sup>) =  $10.71 \pm 0.048 - (19,560 \pm 110/2.3RT)$ .

For the short series of hydrocarbons, isobutane, n-butane, and neopentane, the activation energies for hydrogen abstraction by difluoroamino-radicals ( $E_{\text{NF}_2}$ ) were found<sup>1</sup> to be related to the strengths of the appropriate bonds ( $D[\text{C-H}]$ ) by the Polanyi equation

$$E_{\text{NF}_2} = 1.00[D(\text{C-H}) - 72.5].$$

Thus it was deduced that  $D(\text{NF}_2\text{-H}) \geq 72.5$  kcal. mole<sup>-1</sup>, since the proportionality term in the above expression was unity.

For the reactions of difluoroamino-radicals with acetone we have

$$E_2 - E_{-2} = D(\text{CH}_3\text{COCH}_2\text{-H}) - D(\text{NF}_2\text{-H}),$$

where  $E_{-2}$  is the activation energy for the reverse of reaction (2), *i.e.*, reaction of acetyl radicals with difluoroamine. Thus

$$D(\text{CH}_3\text{COCH}_2\text{-H}) \leq E_2 + D(\text{NF}_2\text{-H})$$

and since  $E_2$  is 19.6 the maximum value of  $D(\text{CH}_3\text{COCH}_2\text{-H})$  is 92.1 kcal. mole<sup>-1</sup>. This, however, must be close to the actual value, since any activation energy for the reverse reaction ( $E_{-2}$ ) may be compensated for by the fact that  $D(\text{NF}_2\text{-H})$  is a minimum value by a similar activation energy term. It, therefore, seems reasonable to conclude that  $D(\text{CH}_3\text{COCH}_2\text{-H}) = 92.1 \pm 1$  kcal. mole<sup>-1</sup>.

The heat of formation of the acetyl radical can now be calculated from the equation

$$D(\text{CH}_3\text{COCH}_2\text{-H}) = \Delta H_f^\circ(\text{CH}_3\text{COCH}_2\cdot) + \Delta H_f^\circ(\text{H}\cdot) - \Delta H_f^\circ(\text{CH}_3\text{COCH}_3)$$

and since  $\Delta H_f^\circ(\text{CH}_3\text{COCH}_3) = -51.8$  kcal. mole<sup>-1</sup> this gives  $\Delta H_f^\circ(\text{CH}_3\text{COCH}_2\cdot) = -11.7$  kcal. mole<sup>-1</sup>. Similarly, the strength of the bond  $\text{CH}_3\text{-COCH}_2\cdot$  can be calculated from the equation

$$D(\text{CH}_3\text{-COCH}_2\cdot) = \Delta H_f^\circ(\text{CH}_3\cdot) + \Delta H_f^\circ(\text{CH}_2\text{CO}) - \Delta H_f^\circ(\text{CH}_3\text{COCH}_2\cdot)$$

Substituting the values  $\Delta H_f^\circ(\text{CH}_3\cdot) = 33.9$  and  $\Delta H_f^\circ(\text{CH}_2\text{CO}) = -14.6$  kcal. mole<sup>-1</sup> yields  $D(\text{CH}_3\text{-COCH}_2\cdot) = 31.0$  kcal. mole<sup>-1</sup>. The activation energy for the addition of methyl radicals to keten is unknown, but a value of  $\geq 31$  kcal. mole<sup>-1</sup> for the decomposition of the acetyl radical seems reasonably in line with results on other radical decompositions.<sup>3</sup>

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<sup>3</sup> J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Pergamon, Oxford, 1961, p. 122.