it is smaller for the planar ring model, larger for the chair conformation.

The differences between the three models which fit the diffraction data for $B_3N_4H_7$ equally well must be regarded as an indeterminancy of the experiment. As pointed out above, all of the fitted parameters, except the angles determining the degree of planarity of the ring, are very nearly equal for the three models. Comparison of the long nonbonded distances in the molecule for the different models gives some indication of shrinkage effects which are only slightly larger than for benzene[18]. The listing in Table IV documents the argument that the degree of departure from planarity for the average structure, within the limits allowed by models B and C, is inherent to the electron-diffraction technique since the differences observed in the across-the-ring distances between the three models are comparable to the experimental errors. We conclude that in B-monoaminoborazine the borazine ring and the amine nitrogen are essentially coplanar, with the amine hydrogens definitely not in this plane.

Acknowledgments. We wish to thank Mr. Richard Hilderbrandt for his technical assistance in obtaining the diffraction patterns. This work was supported by the Advanced Research Projects, the Army Research Office-Durham, and the National Science Foundation.

---

(18) W. V. F. Brooks, B. N. Cyvin, S. J. Cyvin, P. C. Kvande, and E. Meisingseth, *Acta Chem. Scand.*, 17, 345 (1963).

Kinetics of the Reaction of Hydrogen Iodide with 1,1-Difluoroethylene

T. S. Carlton, A. B. Harker, W. K. Natale, R. E. Needham,
R. L. Christensen, and J. L. Ellenson

Contribution from the Department of Chemistry,
Oberlin College, Oberlin, Ohio 44074. *Received April 11, 1968*

Abstract: The gas-phase reaction of hydrogen iodide with 1,1-difluoroethylene produces 1,1-difluoro-1-iodoethane, 1,1-difluoroethane, and iodine. 1,1-Difluoro-2-iodoethane rarely is observed, and never below 230°. The activation energy for consumption of 1,1-difluoroethylene is 27.2 ± 0.7 kcal/mole, and the preexponential factor is 1.5×10^8 l./(mol sec). These values are close to those for the reaction of hydrogen iodide with ethylene. The predominant orientation of hydrogen iodide addition is in keeping with an ion-pair model of the transition state. Calculations based on a point-dipole transition-state model lead to the incorrect prediction that the hydrogen iodide addition is anti-Markovnikov. In the reaction of hydrogen iodide with fluoroethylene, silicon tetrafluoride is produced at both 175 and 305°. Apparently hydrogen fluoride is the product of a side reaction.

Hydrogen iodide reacts with olefins in the gas phase to produce alkyl iodides.[1] Methyl groups adjacent to the double bond have a pronounced effect on the orientation and activation energy of hydrogen iodide addition. The present investigation was undertaken to determine the effects of fluorine substitution adjacent to the double bond. Knowledge of these effects would shed light on the reaction's transition state, which is also the transition state for the reverse reaction, namely dehydroiodination. Relationships between activation energy and structure are known for gas-phase dehydrohalogenations of organic chlorides, bromides, and iodides,[2] but the effects of fluorine substitution on dehydrohalogenation have not been studied.

Experimental Section

Anhydrous hydrogen iodide (Matheson) was degassed and then was freed of iodine and silicon tetrafluoride by bulb-to-bulb distillation from a Dry Ice bath to a *n*-pentane slush. Fluoroethylene, 1,1-difluoroethylene, 1,1-difluoroethane (all from Matheson), and fluoroethane (Air Products) were degassed and then were used without further purification, as no impurities were observed in infrared and gas chromatographic analyses. Authentic samples of 1-fluoro-1-iodoethane and 1,1-difluoro-1-iodoethane were prepared by allowing hydrogen iodide to react at room temperature with fluoroethylene and 1,1-difluoroethylene, respectively. 1,1-Difluoro-2-iodoethane was prepared by heating 2,2-difluoroethyl *p*-toluenesulfonate with sodium iodide in ethylene glycol.[3] The structures of the three organic iodides were verified by their proton nmr splitting patterns.[4] The infrared frequencies of 1,1-difluoro-1-iodoethane agree with previously published values,[5] and those of 1,1-difluoro-2-iodoethane were also determined.[6]

Reactions were carried out in 0.1-l. borosilicate glass vessels, which contained a few glass balls to permit thorough mixing of the reactants. The vessels were flamed while being evacuated to remove water from the inner surface. Stopcocks with Apiezon H grease were the most suitable vessel closures. Reactant pressures were measured with a fused silica spiral manometer sensitive to 0.05 torr. A molten salt bath maintained reaction temperatures constant to

---

(1) P. S. Nangia and S. W. Benson, *J. Chem. Phys.*, 41, 530 (1964), and references cited therein.

(2) A. Maccoll, *Advan. Phys. Org. Chem.*, 3, 91 (1965).

(3) G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Am. Chem. Soc.*, 75, 5978 (1953).

(4) Observed nmr parameters. Chemical shifts are relative to tetramethylsilane. $CHFICH_3$: $J_{HH} = 5.5$, $J_{H1F1} = 49$, $J_{H2F1} = 20$ cps. CF_2ICH_3: δ -2.49 ppm; $J_{HF} = 17$ cps. CHF_2CH_2I: δ_{H1} -5.79, δ_{H2} -3.39 ppm; $J_{HH} = 4$, $J_{H1F1} = 57$, $J_{H2F1} = 16$ cps.

(5) M. Hauptschein, A. H. Fainberg, and M. Braid, *J. Org. Chem.*, 23, 322 (1958). Our frequencies (cm^{-1}) and intensities for CF_2ICH_3: 619 s, 625 s, 632 s, 878 s, 882 s, 888 s, 900 m, 962 s, 1097 vs, 1103 vs, 1107 vs, 1181 vs, 1188 vs, 1387 s, 2943 m, 3015 m (triplet).

(6) CF_2HCH_2I frequencies and intensities: 442 s, 450 s, 540 m, 664 s, 672 s, 702 m, 740 m, 815 m, 975 s, 979 s, 983 s, 1055 vs, 1065 vs, 1115 vs, 1123 vs, 1188 s, 1348 m, 1353 s, 1363 s, 1380 s, 1389 s, 1425 s, 1430 s, 2981 s.

±0.3°, and liquid nitrogen was used to quench the reactions.

In preparation for gas chromatographic analysis the reaction mixture was separated into a fraction volatile at the temperature of a *n*-pentane slush (about −130°) and a fraction involatile at that temperature. In the runs with 1,1-difluoroethylene the volatile fraction was analyzed at 0° with a 95 in. × 0.31 in. i.d. column of 14% dimethylsulfolane (tetrahydrodimethylthiophene 1,1-dioxide) on 45–60 mesh Chromosorb P. Retention times were 3.5 min for 1,1-difluoroethylene and 12 min for 1,1-difluoroethane. Hydrogen iodide did not emerge from the column. The fraction involatile at −130° was analyzed at room temperature with a 39 in. × 0.31 in. column of 13% Halocarbon 11-21 (a mixture of saturated chlorofluorocarbons, Halocarbon Products Corp.) on 45–60 mesh Chromosorb P. Retention times were 2 min for 1,1-difluoroethane, 6 min for 1,1-difluoro-1-iodoethane, and 15 min for 1,1-difluoro-2-iodoethane. The flow of nitrogen through the column was about 40 ml/min. A gas density detector was used, and peak areas were compared with those of a known quantity of a reference compound.

Results

A. **Fluoroethylene.** Quantitative studies of the reaction of hydrogen iodide with fluoroethylene were not completed because infrared examination revealed that some silicon tetrafluoride was produced in this system at both 175 and 305°.

B. **1,1-Difluoroethylene.** At low conversions the only observed products of the reaction of hydrogen iodide with 1,1-difluoroethylene were 1,1-difluoro-1-iodoethane, 1,1-difluoro-2-iodoethane, 1,1-difluoroethane, and iodine. 1,1-Difluoro-2-iodoethane was not observed below 230° and rarely was observed above this temperature. When the reaction mixture was frozen with liquid nitrogen, it was always colorless before the reaction and yellow, orange, or brown after the reaction. Presumably this color was due to small amounts of iodine.

In a control run 372 μmoles of hydrogen iodide and 362 μmoles of 1,1-difluoroethylene were mixed in a 110.6-ml reactor. All the mixing, separation, and analysis of a regular run were carried out, but the reaction period at high temperature was omitted. No detectable amounts of any reaction products were formed in this control run.

The following six elementary processes are thought to be the only important ones in this reaction system.

$$CF_2CH_2 + HI \longrightarrow CF_2ICH_3 \qquad (1)$$

$$CF_2ICH_3 + I \longrightarrow CF_2CH_3 + I_2 \qquad (2)$$

$$CF_2CH_3 + HI \longrightarrow CF_2HCH_3 + I \qquad (3)$$

$$CF_2CH_2 + HI \longrightarrow CF_2HCH_2 \text{ (or } CF_2CH_3\text{)} + I \qquad (4)$$

$$CF_2HCH_2 + HI \longrightarrow CF_2HCH_3 + I \qquad (5)$$

$$2I + M \longrightarrow I_2 + M \qquad (6)$$

The 1,1-difluoroethane and iodine may have been formed by a mechanism consisting of reactions 1, 2, 3, and 6 and by a second mechanism consisting of reactions 4, 3, 5, and 6. Since reaction 4 is the rate-determining step of the latter mechanism and since the product of reaction 1 either remains as 1,1-difluoro-1-iodoethane or is converted to 1,1-difluoroethane, these mechanisms lead to the rate expression

$$\frac{d[CF_2CH_2]}{dt} = -(k_1 + k_4)[CF_2CH_2][HI] \qquad (7)$$

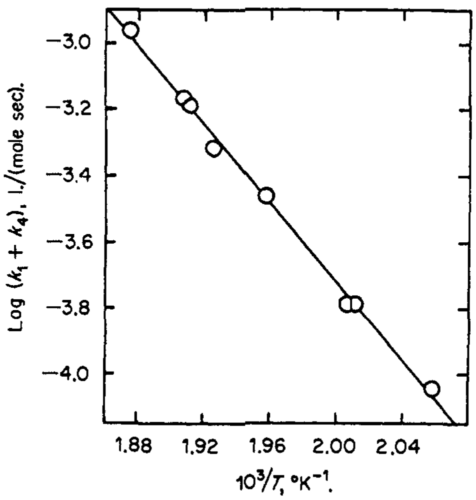

Figure 1. Arrhenius plot of $k_1 + k_4$.

A molecule of 1,1-difluoro-1-iodoethane or 1,1-difluoroethane is formed for every molecule of 1,1-difluoroethylene that is consumed. Therefore if the concentrations of 1,1-difluoroethylene and hydrogen iodide depart only negligibly from their initial values, $[CF_2CH_2]_i$ and $[HI]_i$, the value of $k_1 + k_4$ equals

$$([CF_2ICH_3]_f + [CHF_2CH_3]_f)/(t[CF_2CH_2]_i[HI]_i)$$

where the reaction duration is t, and the subscript f indicates concentration when the reaction is quenched. This expression for $k_1 + k_4$ is accurate to within 1% when applied to our experiments. An even more accurate expression is obtained by using the approximate average concentrations

$$[CF_2CH_2]_i - ([CHF_2CH_3]_f + [CF_2ICH_3]_f)/2$$

and

$$[HI]_i - [CHF_2CH_3]_f - [CF_2ICH_3]_f/2$$

in place of $[CF_2CH_2]_i$ and $[HI]_i$. These corrections to the reactant concentrations were used in calculating the values of $k_1 + k_4$ shown in Table I and Figure 1. No 1,1-difluoro-2-iodoethane was detectable in the tabulated runs. The activation energy is 27.2 ± 0.7 kcal/mole, and the preexponential factor, A, is 1.5 × 10^8 l./(mole sec) (log A = 8.17 ± 0.28).

Table I. Kinetic Data[a]

		Initial μmoles		Final μmoles		
Temp, °C	Time, min	HI	CH_2-CF_2	CH_3-CF_2I	CH_3-CHF_2	$k_1 + k_4$, l./(mole sec)
212.6	120	182.3	347.6	0.163	0.272	9.0 × 10^{-5}
246.3	54.5	233.4	250.9	0.147	0.825	4.8 × 10^{-4}
224.1	95	382.7	153.6	0.063	0.430	1.63 × 10^{-4}
260.1	57	109.3	408.1	0.070	1.41	1.09 × 10^{-3}
237.9	117	117.3	455.3	0.119	1.04	3.46 × 10^{-4}
225.3	90	123.3	529.9	0.105	0.412	1.63 × 10^{-4}
251.0	32.0	358.8	477.0	0.107	1.91	6.8 × 10^{-4}
250.2	153.5	104.4	387.9	0.02	2.17	6.5 × 10^{-4}

[a] The reactor volume was 94.4 ml in the first two runs and 110.6 ml in all others. In the first two runs the surface-to-volume ratio was three to four times larger than in the other runs.

A slight amount of iodine was present at the start of the third run only. Addition of solid iodine at the beginning of a run at 207° caused the apparent rate constant to be at least twice as large as its expected value at that temperature. At temperatures below 200° the rate constants were unreproducible and were always higher than those predicted by extrapolation of the straight line in Figure 1.

Table II shows results for reactions in which only hydrogen iodide and 1,1-difluoro-1-iodoethane were present initially. These runs were performed in a 110.6-ml reactor, and the temperatures are uncertain by 2°.

Table II. Reaction of CF_2ICH_3 with HI

Temp, °C	Time, min	Initial μmoles HI	Initial μmoles CF_2-ICH_3	Final μmoles CF_2-ICH_3	Final μmoles CHF_2-CH_3
222	90	123	1.23	0.96	0.21
240	117	187	1.16	0.26	0.84
261	57	103	1.67	0.21	1.53

Discussion

A. **Fluoroethylene.** The production of silicon tetrafluoride indicates that hydrogen fluoride was produced in a side reaction. Bose and Benson likewise observed hydrogen chloride in the reaction of hydrogen iodide with chloroethylene.[7] They presented evidence for their proposal that hydrogen chloride was produced in an iodine-atom-catalyzed elimination from chloroethane. An iodine-catalyzed elimination from fluoroethane was not, however, the source of hydrogen fluoride in the fluoroethylene system. Little iodine was present at any time during the reaction at 175°, and silicon tetrafluoride was not found when fluoroethane and iodine were heated together at 175°.

B. **1,1-Difluoroethylene.** Above 200° the reaction of hydrogen iodide with 1,1-difluoroethylene was homogeneous and satisfied eq 7. The rate enhancement and scatter below 200° may indicate that a heterogeneous reaction occurred at these lower temperatures, perhaps because enough water adhered to the vessel walls to stabilize carbonium ions even though the vessels were flamed before use. The absence of an appreciable contribution by a heterogeneous reaction in the temperature range of Figure 1 is indicated by the insensitivity of the rate to a change in the surface-to-volume ratio of the reaction vessel. Nangia and Benson found that iodine atoms catalyzed the addition of hydrogen iodide to 2-butene,[1] and we found that large amounts of iodine increased the apparent rate constant. The much smaller amounts of iodine in normal runs did not cause any detectable rate increase. There is little scatter in Figure 1 despite the varying amounts of 1,1-difluoroethane and therefore of iodine that were formed in the several runs. Furthermore, in the third run only, a slight amount of iodine was present in the reaction mixture from the start, yet agreement with the other runs was good.

The experimental results do not indicate whether most of the 1,1-difluoroethane was formed *via* reaction 1 or reaction 4. The latter reaction cannot be ruled out, since ΔH for the corresponding reaction of ethylene is only 32.8 kcal/mole,[8] and the activation energy for reaction 4 might be as low as 27 kcal/mole, the activation energy for consumption of 1,1-difluoroethylene. On the other hand, both Arrhenius parameters for the reaction of hydrogen iodide with ethylene are strikingly close to those measured in the present investigation,[9] and the ethylene reaction is thought to proceed primarily *via* the step corresponding to reaction 1.[8] The results in Table II show that 1,1-difluoro-1-iodoethane does form 1,1-difluoroethane at temperatures and hydrogen iodide concentrations that are representative of those in Table I. This reaction is autocatalyzed and must involve an induction period in which catalytic iodine is being formed. In the presence of 1,1-difluoroethylene reaction 4 would produce iodine and thereby shorten this induction period. Consequently the conversions of 1,1-difluoro-1-iodoethane in Table II are lower limits for the conversions in the presence of 1,1-difluoroethane.

The uncertainty about the importance of reaction 4 keeps us from assigning the measured Arrhenius parameters to reaction 1. Nevertheless the activation energy for reaction 1 must be lower than that for reaction 8. 1,1-Difluoro-2-iodoethane was observed only rarely,

$$CF_2CH_2 + HI \longrightarrow CF_2HCH_2I \tag{8}$$

and it was never detectable below 230°. These facts require that E_1 be less than E_8 unless A_1 is much larger than A_8 or reaction 2 proceeds much more slowly than the corresponding reaction of 1,1-difluoro-2-iodoethane; both of these conditions are improbable.

The virtual absence of 1,1-difluoro-2-iodoethane from the reaction products allows us to exclude reactions 9 and 10 from the mechanism. Analogies with reactions

$$CF_2CH_3 + I_2 \longrightarrow CF_2ICH_3 + I \tag{9}$$

$$CF_2HCH_2 + I_2 \longrightarrow CF_2HCH_2I + I \tag{10}$$

of trifluoromethyl and methyl suggest that k_9 and k_{10} are almost equal, and it would be surprising if reaction 4 produced CF_2CH_3 a great deal faster than CF_2HCH_2, or if reaction 2 were a great deal slower than the corresponding reaction of 1,1-difluoro-2-iodoethane. Under the conditions of Table I the concentrations of iodine, CF_2CH_3, and CF_2HCH_2 are evidently too low to permit reactions 9 and 10 to compete effectively with reaction 1.

Two models have been proposed for the transition state of alkyl halide dehydrohalogenation reactions and nonradical additions of hydrogen halides to olefins. Maccoll's ion-pair model consists of a closely associated halide ion and carbonium ion.[2,10,11] Maccoll cites two kinds of evidence in support of the ion-pair model. Qualitative support is provided by the parallel effect of substituents on the rates of gas-phase dehydrohalogenation reactions and the rates of SN1 and E1 reactions in polar solvents. Quantitative support is provided by a linear relationship between the activation energies for dehydrohalogenation reactions and the heterolytic bond dissociation energies of the carbon–halogen bonds.[11] The ion-pair model is consistent with our results, for 1,1-difluoro-1-iodoethane is formed more

---

[7] A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **38**, 878 (1963).

[8] S. W. Benson and A. N. Bose, *ibid.*, 37, 2935 (1962).

[9] According to ref 8, E_a = 28.9 kcal/mole and $A = 3.3 \times 10^8$ l./(mole sec) for the addition of hydrogen iodide to ethylene.

[10] A. Maccoll, "Theoretical Organic Chemistry," Butterworth & Co., Ltd., London, 1959, p 230.

[11] A. Maccoll, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 159.

readily than 1,1-difluoro-2-iodoethane in the gas-phase addition of hydrogen iodide to 1,1-difluoroethylene. The former iodide is the only product of the same reaction in the dark at 20° in anhydrous liquid hydrogen iodide, in which the reaction is almost certainly ionic.[12] Presumably $CH_3CF_2^+$ is more stable than $CHF_2CH_2^+$ because of stabilization by such resonance structures as $CH_3CF{=}F^+$. Unfortunately, a quantitative test of the model against our results is not possible at present.

The other transition-state model is the point-dipole model of Benson, Bose, and Haugen.[13,14] In this model the bonds that are being broken are treated as point dipoles located at the bond centers. The calculated activation energy is quite sensitive to the assumed values of bond lengths at the reaction site, but a uniform and reasonable basis for choosing these and other parameters leads to good predictions for 15 or more addition reactions between hydrogen halides and unsaturated hydrocarbons.[14]

Calculations of activation energies for reactions 1 and 8 require that the point-dipole model be augmented to take into account the polar carbon–fluorine bonds. Our calculations are based on the following models for 1,1-difluoroethylene and the activated complexes. The model for 1,1-difluoroethylene has a point dipole called the CF_2 dipole, with value μ_1, which is the resultant of the two CF bond dipoles and which therefore lies on the C–C axis at a distance r beyond the fluorinated carbon. The model also has a CC point dipole, with value μ_2, which is halfway between the carbon atoms,[15] has its positive end toward the fluorinated carbon, and therefore is antiparallel to the CF_2 dipole.[16] The scalar difference $\mu_1 - \mu_2$ equals 1.37 D, the experimental dipole moment of 1,1-difluoroethylene.[17] The model for the activated complex has the same geometry for hydrogen iodide and the two carbons as in Figure 2 of ref 14. The CC and HI point dipoles in the activated complex have the same magnitudes, μ_3 and μ_4, respectively, as in ref 14, and they are at the centers of their respective bonds and parallel to these bonds. The CF_2 dipole still has the value μ_1 and is still at a distance r from the fluorinated carbon. The CF_2 dipole is coplanar with the H–I and C–C bonds and is on and parallel to a line that passes through the fluorinated carbon and makes an angle θ with the C–C bond.

The calculated activation energy at 0°K is the sum of the energies for the following processes: (a) removing the CF_2 dipole to infinity; (b) discharging the CC dipole from μ_2 to zero; (c) recharging the CC dipole from zero to μ_3; (d) discharging the HI dipole from 0.382 D to zero; (e) recharging the HI dipole from zero to μ_4; (f) bringing the HI dipole from infinity to its position and orientation in the activated complex; and (g) bringing the CF_2 dipole from infinity to its position and orientation in the activated complex. The calculated energies for processes b, c, d, and e depend on the longitudinal polarizability of the olefin and of hydrogen iodide. Calculations based on a table of anisotropic bond polarizabilities indicate that the longitudinal polarizability of 1,1-difluoroethylene is only about 3% greater than that of ethylene.[18] Our calculations ignore altogether this slight difference and use the same polarizabilities as were used in calculations on hydrogen iodide addition to ethylene.[14] The energies for processes c–e have the same values as in ref 14, and the energy of process f is 0.857 times the corresponding energy from that reference.[19] The sum of energies c–f, 31.3 kcal/mole, is the calculated activation energy for addition of hydrogen iodide to ethylene. The energies for processes a and b depend only on the value of r and of μ_2 (since $\mu_1 = \mu_2 + 1.37$ D). The energy for process g depends on r, θ, μ_2, and whether the activated complex is for 1,1-difluoro-1-iodoethane or 1,1-difluoro-2-iodoethane formation.

The calculated activation energies for reactions 1 and 8 are shown in Table III. A value of 0.76 Å for r corresponds to locating the CF bond dipole at the nucleus of the fluorine atom. A value of 55° for θ corresponds to sp^3 hybridization about the fluorinated carbon. Larger values of r or θ are physically unreasonable. Any reasonable values for r, θ, and μ_2 yield the incorrect predictions that E_1 is larger than E_8 and that E_8 is negative. Thus a point-dipole model in which the CF_2 dipole remains fixed in magnitude and in its distance from the carbon atom is unsatisfactory, whereas allowing these two quantities to change in going from the reactant olefin to the transition state would make the model too flexible to be of predictive value.

Table III. Calculated Activation Energies for Reactions 1 and 8

r, Å	θ, deg	μ_2, D	E_a, kcal/mole	
			CH_3CF_2I	CHF_2CH_2I
0.38	0	0.00	141	−73
0.38	55	0.00	159	−90
0.38	0	0.50	156	−136
0.38	55	0.50	182	−159
0.38	0	1.00	157	−213
0.76	0	0.00	77	−10
0.76	55	0.00	87	−19
0.76	0	0.50	84	−34
0.76	0	1.00	86	−64
0.76	55	1.00	102	−80

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Assistance was also received from the National Science Foundation through its Undergraduate Research Participation program. We wish to thank Mr. F. L. Roe, Jr., and Mr. T. C. Frankiewicz for conducting preliminary investigations which assisted this research.

---

(12) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 61 (1956).

(13) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, 39, 3463 (1963).

(14) S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, 87, 4036 (1965).

(15) The carbon atoms are 1.31 Å apart: V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, 38, 2693 (1963).

(16) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, 89 4253 (1967).

(17) A. Roberts and W. F. Edgell, *J. Chem. Phys.*, 17, 742 (1949).

(18) R. J. W. Le Fevre, *Advan. Phys. Org. Chem.*, 3, 1 (1965).

(19) The present calculations include a factor for the angular dependence of each dipole–dipole interaction energy. For process f this factor is 0.857.