Ionic Chain Mechanism. The compounds CsF and perhaps RbF will separate preferentially into ions rather than atoms. Moreover, if exothermic ion-molecule reactions have small activation energies, the chain

$$F^- + LiCl \longrightarrow LiF + Cl^- \qquad \text{(II-7)}$$

$$Cl^- + CsF \longrightarrow CsCl + F^- \qquad \text{(II-8)}$$

will have an apparent activation energy about 10 kcal/mole less than that for the equivalent chain involving atoms instead of ions. Hence the over-all process $LiCl + CsF \rightarrow LiF + CsCl$ might well proceed by an ionic rather than by an atomic chain mechanism.

Since preferential dissociation into ions rather than atoms appears to be a property unique to one or two compounds, and since ionic chains are not apt to be sufficiently faster to be preferred in the reactions of other compounds, this mechanism does not warrant general consideration.

Triatomic Molecule Mechanisms. The discussion has specifically excluded consideration of mechanisms involving triatomic molecules. Such a mechanism might be

$$MN + PQ \longrightarrow M + PQN \qquad \text{(II-9)}$$

$$M + PQN \longrightarrow MP + NQ \qquad \text{(II-10)}$$

These mechanisms are probably unimportant in systems containing only hydrogen, halogens, and alkali metal atoms. However, they may be preferred paths for some reactions in systems containing carbon, nitrogen, and oxygen.

Reactions of Diatomic Molecules. II. Predictions and Comparisons with Experiment

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Received October 28, 1965

Abstract: Procedures developed in the previous paper have been used to estimate rates and mechanisms for 110 possible reactions of diatomic molecules, 47 of which involve net chemical change. For only 20 of these reactions do there appear to be experimental observations of mechanistic significance, but in all except perhaps one or two of these 20 examples kinetic and mechanistic predictions are in agreement with experiment or discrepancies can be rationalized. More experimental work is desirable, particularly for reactions by bimolecular mechanisms. The following mechanistic predictions are made. Isotopic scrambling for the elements H, Li, Na, K, and probably N and O, will proceed by atomic chain mechanisms under experimentally attainable conditions. Isotopic scrambling of the elements F, Cl, Br, and I will proceed by bimolecular mechanisms. Iodine is the only halogen that will react with hydrogen preferentially by a bimolecular mechanism, but it may be possible to detect a contribution from this mechanism in the bromine reaction. All halogen-halogen reactions will proceed by bimolecular mechanisms. The two mechanistic types are of comparable probabilities for reactions of halogens with hydrogen halides. Symmetrical (exchange) reactions of hydrogen halides with hydrogen and with other hydrogen halides will proceed by atomic chain mechanisms. Chlorine molecules will react with sodium molecules with an activation energy almost as low as that for the reaction with sodium atoms. Nitric oxide will decompose by a bimolecular mechanism, forming $N_2 + O_2$ (or perhaps $N_2O + O$), although an atomic chain mechanism will become dominant at very high temperatures. Mechanisms involving metastable triatomic molecules complicate predictions for other reactions involving carbon, nitrogen, and oxygen.

The previous paper[1] discussed the mechanisms by which diatomic molecules might react and presented general procedures for predicting activation energies. In order to test the reasonableness of these procedures, they have been applied to 110 possible reactions and the results of the calculations have been compared with available experimental data and with calculations on some of the same reactions by Benson and Haugen.[2]

Reactions are grouped by chemical similarity in the following tables and are designated by reactant molecules and classification from the previous paper.[1] For each reaction, generalized as $MN + PQ \rightarrow MP + NQ$, the energy as a function of extent of reaction, x, was computed in 0.100 intervals from

$$E_x = -D_x^c(\mathrm{MP}) - D_x^c(\mathrm{NQ}) - D_{1-x}^c(\mathrm{MN}) - D_{1-x}^c(\mathrm{PQ}) \qquad (1)$$

with the use of Table IV of the previous paper.[1] The three values nearest the maximum were fitted to a quadratic function to calculate $x^{\ddagger}$ (the value at that maximum) and the activation energy, E_m.

The tables also contain values of $\frac{1}{2}D_0^\circ + E_c$, the effective activation energy for the atomic chain mechanism according to the kinetics of Appendix I of the previous paper.[1]

If a reaction appeared to be of potential experimental interest, entropies of transition states were estimated by use of the assumptions in Appendix I. These were used to calculate T_r, the temperature at which the initial rate by the fastest mechanism is 10^{-6} mole/l. sec when the concentrations of both reactants[3] are 0.0100

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[1] R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4311 (1966).

[2] S. W. Benson and G. R. Haugen, *ibid.*, **87**, 4036 (1965).

mole/l. This calculation indicates the temperature region for study by conventional gas kinetic procedures.

The penultimate column in most tables is log Q_r, where Q_r is the value of v_c/v_m at T_r when reactants are at concentrations[3] of 0.0100 mole/l. A positive log Q_r indicates that the atomic chain mechanism is dominant.

If Benson and Haugen[2] independently estimated activation energy for a bimolecular mechanism, their value is reported as E_{BH} in the final column.

Results of Calculations

Isotopic Scrambling (S1) Reactions. Calculations for several elements are presented in Table I. The mechanism is known only for hydrogen. Theories that regard activation energy for the bimolecular mechanism as a constant fraction of bond energy would predict the same mechanism for all other elements, but Table I disagrees with that conclusion.

Table I. Kinetics of Isotopic Scrambling (S1) Reactions

No.	Element	E_m, kcal/mole	$^1/_2D_0{}^\circ + E_c$, kcal/mole	T_r, °K	log Q_r	E_{BH}, kcal/mole
1a	H	85.2	57.6	823	10.77[a]	60.7
1b	F	9.7	22.0	223	−7.84	
1c	Cl	16.5	31.5	380	−4.96	
1d	Br	10.4	25.7	250	−9.57	
1e	I	6.7	20.8	165	−14.65	
1f	Li	16.7	16.5	261	2.80	
1g	Na	10.1	11.6	194	0.53	
1h	K	5.6	8.9	118	−3.79	
1i	N	111.0	116.5	1840	3.10	
1j	O	51.2	63.0	1100	1.08	

[a] The conclusions of A. Farkas and L. Farkas (*Proc. Roy. Soc.* (London), **A152,** 124 (1935)) indicate a k_c at 807°K almost exactly equal to that from these calculations.

The scrambling reactions of oxygen and nitrogen require high temperatures but are possible to study. Those of chlorine and bromine are possible in principle but would be very difficult. Fluorine and iodine have only one stable isotope, but scrambling in fluorine might be observed by a nuclear resonance technique. Under any conditions attainable experimentally, the alkali elements should undergo rapid isotopic scrambling by the atomic chain mechanism.

Hydrogen–Halogen Reactions. The possible reactions of different halogens with hydrogen are presented in Table II.

The calculations for the bromine reaction (2b) suggest that a contribution from the bimolecular mechanism might possibly be detected at high bromine concentrations and low temperatures. Detection would be facilitated if toluene, diphenylmethane, or some similar scavenger could be found to react irreversibly with bromine atoms.

Chain reactions of interhalogen compounds (2e to 2j) are potentially complicated. Thus the reaction $H + IBr \rightarrow HBr + I$ would be virtually chain terminating, and Müller[4] found that addition of iodine did indeed slow the reaction of hydrogen with bromine.

Bonner, *et al.*,[5] claimed that iodine chloride reacted with hydrogen (2f) by a bimolecular mechanism with an activation energy of 33.9 kcal/mole, in disagreement with the predictions of Table II. The rapid subsequent reaction $HI + ICl \rightarrow HCl + I_2$ was invoked to explain the observed products. However, the equilibrium $2ICl \rightleftarrows I_2 + Cl_2$ should be established rapidly in this system, and the rate of reaction 2c by the atomic chain mechanism should be proportional to [ICl] with apparent activation energy 34.9 kcal/mole, in good agreement with the observations of Bonner, *et al.*[5] This reinterpretation predicts that the rate should be somewhat retarded by added iodine in apparent contradiction with the observations. The system deserves further study.

Halogen–Halogen Reactions. The calculations predict that the highly polarizable halogen molecules will always react with each other by bimolecular mechanisms. Table III is concerned with reactions forming interhalogen compounds from the elements. Although the very limited data on reactions 3a and 3c seem to support the prediction of bimolecular mechanisms, much more experimental work is needed before the general prediction is established.

Table IV contains calculated activation energies by the bimolecular mechanism for the possible symmetrical and unsymmetrical halogen–halogen reactions involving no more than three different elements. All unsymmetrical activation energies are computed for the exothermic direction, which belongs to type U2α or U3α unless otherwise indicated.

The entries in Table IV show some interesting trends, although it would be difficult to test the predictions for reactions not also included in Tables I or III. If only the three heavier elements are present, substitution of a lighter for a heavier halogen invariably raises the activation energy. If fluorine is present, the effect of a substitution is less certain, and the above generalization fails badly if the number of adjacent fluorines is increased by such a substitution. Apparently the repulsions causing the low bond energy in elemental fluorine also influence reactions involving this molecule. For 15 of the 18 pairs of isomeric transition states, the one leading to symmetrical reaction (atoms of the same element on opposite corners) has a lower energy than that leading to unsymmetrical reaction (like atoms on adjacent corners). For the three exceptions (I_2BrF, Br_2ICl, and Cl_2BrF), the difference is less than 1 kcal/mole. Since formation of an interhalogen compound from the elements is invariably exothermic, it is not surprising that transition states favor juxtaposition of nonidentical species.

Halogen–Hydrogen Halide Reactions. Possible reactions of halogens with hydrogen halides are presented in Table V. Although unsymmetrical "displacement" reactions of the type $2HX + Y_2 \rightarrow 2HY + X_2$ must have been favored experiments in aqueous solution for as long as chemistry has been a recognized part of the high school curriculum, gas-phase studies seem to be virtually nonexistent. Studies of symmetrical reactions by isotopic exchange are little more extensive.

The calculations predict a pattern of rates and mechanisms that is internally consistent and readily rational-

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(3) For S1 and S2β reactions, the rate is for 0.0100 mole/l. of the only molecular species present. The rate for all symmetrical (S) reactions is that for reaction if all atoms of the same element are behaving identically.

(4) W. Müller, *Z. Elektrochem.*, **30,** 416 (1924); *Z. Physik. Chem.*, **123,** 1 (1926).

(5) W. D. Bonner, W. L. Gore, and D. M. Yost, *J. Am. Chem. Soc.*, **57,** 2723 (1935).

Table II. Kinetics of Hydrogen–Halogen Reactions

No.	Reactants	Reaction class	$x^{\ddagger}$	E_m, kcal/mole	$^1/_2D_0{}^\circ + E_c$, kcal/mole	T_r, °K	log Q_r	E_{BH}, kcal/mole
2a	$H_2 + I_2$	U2α	0.449	(41.4)[a]	52.5	710	−0.52[b]	44.5
2b	$H_2 + Br_2$	U2α	0.407	39.3	41.5	576	2.28[c]	52.5
2c	$H_2 + Cl_2$	U2α	0.384	38.9	31.6	440	7.12[d]	57.3
2d	$H_2 + F_2$	U2α	0.253	21.7	20.0	275	4.31[e]	99.9
2e	$H_2 + IBr$	U3α	0.431	41.0	39.7	*f*	*f*	45.9
2f	$H_2 + ICl$	U3α	0.422	41.6	27.9	*f*	*f*	47.3
2g	$H_2 + BrCl$	U3α	0.397	39.6	29.1	*f*	*f*	51.0
2h	$H_2 + IF$	U3α	0.354	33.2	24.8	*f*	*f*	
2i	$H_2 + BrF$	U3α	0.355	35.2	29.5	*f*	*f*	62.5
2j	$H_2 + ClF$	U3α	0.340	35.8	32.2	*f*	*f*	74.3

[a] Experimental value used to evaluate parameter *ff*. [b] Experimental value (J. H. Sullivan, *J. Chem. Phys.*, **30**, 1292 (1959)) of log Q_r is −2.05. Rate of atomic chain mechanism is one-seventh of that calculated here and rate of bimolecular mechanism is five times that calculated. [c] Experimental rate (G. C. Fettis and J. H. Knox, *Progr. Reaction Kinetics*, **2**, 1 (1964)) (atomic chain) is 1.5 times that calculated here. [d] Experimental rate (Fettis and Knox[c]) (atomic chain) is one-thirteenth of that calculated here. [e] Oxygen inhibited reaction is claimed to go by atomic chain mechanism (J. B. Levy and B. K. W. Copeland, *J. Phys. Chem.*, **69**, 408 (1965)) and uninhibited reaction should favor this mechanism even more. [f] Additional possible reactions complicate this system.

Table III. Kinetics of Interhalogen Formation (U2α) Reactions

No.	Reactants	$x^{\ddagger}$	E_m, kcal/mole	$^1/_2D_0{}^\circ + E_c$, kcal/mole	T_r, °K	log Q_r	E_{BH}, kcal/mole
3a	$I_2 + Br_2$	0.429	7.5	23.3	176	−15.92[a]	40.2
3b	$I_2 + Cl_2$	0.418	9.0	27.2	204	−15.80	44.7
3c	$Br_2 + Cl_2$	0.482	13.2	29.7	294	− 8.77[b]	52.9
3d	$I_2 + F_2$	0.206	2.3	19.8	56	−65.6	
3e	$Br_2 + F_2$	0.206	3.2	20.0	72	−47.3	96.3
3f	$Cl_2 + F_2$	0.266	5.9	20.0	132	−19.64	101.3

[a] Reaction in carbon tetrachloride fits bimolecular kinetics and at 25° is three times as fast as calculated here (P. R. Walton and R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4324 (1966)). [b] Claimed to be instantaneous in ether and chloroform but to have a time lag of several seconds in carbon tetrachloride (S. Barrat and C. P. Stein, *Proc. Roy. Soc.* (London), **A122**, 582 (1929)). Gas phase measurements (W. Jost, *Z. Physik. Chem.*, **B14**, 413 (1931); G. Brauer and E. Victor, *Z. Elektrochem.*, **41**, 508 (1935)) consistent with bimolecular mechanism with estimated activation energy (Jost) of 14 kcal/mole. Reaction in sulfuric acid goes by nonradical (but perhaps ionic) mechanism with activation energy of 18 kcal/mole (P. R. Walton and R. M. Noyes, to be published).

Table IV. Predicted Activation Energies for Bimolecular Symmetrical and Unsymmetrical Halogen–Halogen Reactions

Formula of transition state	$E_m{}^S$, kcal/mole	$E_m{}^U$, kcal/mole	Formula of transition state	$E_m{}^S$, kcal/mole	$E_m{}^U$, kcal/mole
I_4	6.7		Cl_4	16.5	
I_3Br	7.9		Cl_3I	14.5	
I_3Cl	9.6		Cl_3Br	15.5	
I_3F	8.1		Cl_3F	18.2	
I_2Br_2	9.1	7.5	Cl_2F_2	19.9	5.9
I_2Cl_2	12.6	9.0	Cl_2IBr	13.5	11.8
I_2F_2	9.6	2.3	Cl_2IF	16.2	11.1
I_2BrCl	10.8	8.9	Cl_2BrF	17.2	16.4
I_2BrF	9.3	8.8[a]	F_4	9.7	
I_2ClF	11.1	11.7[a]	F_3I	9.6	
Br_4	10.4		F_3Br	12.8	
Br_3I	9.8		F_3Cl	14.8	
Br_3Cl	12.5		F_2IBr	12.7	3.2
Br_3F	13.2		F_2ICl	14.7	5.0
Br_2Cl_2	14.5	13.2	F_2BrCl	17.8	4.8
Br_2F_2	15.9	3.2			
Br_2ICl	11.8	11.1[a]			
Br_2IF	12.5	8.5			
Br_2ClF	15.2	14.6			

[a] Exothermic unsymmetrical reaction is U3β.

ized. The experimental observations are less clear. The only careful kinetic study indicates that the reaction of Cl_2 + HCl goes by a radical chain mechanism at the rate predicted, but the reaction of Cl_2 + HBr appears to be much faster than can easily be explained and the reaction of Br_2 + HBr is either very fast or heterogeneously induced. More work on such systems is clearly needed.

Other Symmetrical Hydrogen Halide Reactions. Table VI considers other possible exchange reactions of hydrogen halides.

The predictions are in good agreement with experiment except for the claim of Steiner and Rideal[6] that the bimolecular mechanism makes a significant contribution to the HCl catalysis of ortho-para hydrogen conversion (6c). However, these authors admitted that their activation energy led to an encounter diameter of 10 A for the reaction; either they seriously overestimated that activation energy or were looking at an artifact that made about the same percentage contribution at each temperature. Moreover, the principal chain mechanism includes the reaction of chlorine atoms with hydrogen, and this step is notoriously sensitive to impurities like residual oxygen. Finally, no bimolecular contribution was observed[7] when HBr (6b) was substituted for HCl, yet every criterion for estimating rates of bimolecular processes would predict that HBr would react at the same rate or faster. Hence the claim of a significant bimolecular contribution to the HCl reaction must be considered unproved.

Reactions Involving Alkalies. Table VII presents calculations on the possible reactions involving the elements sodium, chlorine, and hydrogen. Values of T_r and Q_r have not been computed because the species do not lend themselves to conventional kinetic studies. Molecular beams may be suitable for testing some of the predictions of this table.

Reactions Involving Carbon, Nitrogen, and Oxygen. Most elements from other than the first and seventh columns of the periodic table do not form stable diatomic molecules whose reactions can be studied by the techniques of gas kinetics. Carbon, nitrogen, and

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(6) See Table VI, footnote *e*.

(7) See Table VI, footnote *d*.

Table V. Kinetics of Halogen–Hydrogen Halide Reactions

No.	Reactants	Reaction class	$x^\ddagger$	E_m, kcal/mole	$^1/_2D_0{}^\circ + E_c$, kcal/mole	T_r, °K	log Q_r	E_{BH}, kcal/mole
5a	$HI + Br_2$	U3α	0.445	21.5	28.3	435	−1.58	42.0
5b	$HI + IBr$	U3β	0.459	21.8	29.3	453	−2.09	35.4
5c	$HI + Cl_2$	U3α	0.416	21.9	38.0	435	−5.85	46.7
5d	$HI + ICl$	U3β	0.439	22.3	40.9	456	−7.33	36.5
5e	$HBr + Cl_2$	U3α	0.470	32.2	35.5	591	1.13^a	52.4
5f	$HBr + BrCl$	U3β	0.475	31.5	34.7	614	0.59^a	45.8
5g	$HI + F_2$	U3α	0.254	9.1	20.0	185	−9.58	
5h	$HI + IF$	U3β	0.328	14.1	34.9	286	−14.02	
5i	$HBr + F_2$	U3α	0.306	15.7	20.0	318	0.02	95.5
5j	$HBr + BrF$	U3β	0.402	25.9	39.0	520	−3.76	57.5
5k	$HCl + F_2$	U3α	0.349	23.6	20.0	316	5.48	99.0
5l	$HCl + ClF$	U3β	0.434	36.1	35.7	596	2.49	72.7
5m	$HI^* + I_2$	S2α	0.5	22.5	20.8	363	2.47	33.8
5n	$HBr^* + Br_2$	S2α	0.5	31.5	25.7	442	4.83^b	47.5
5o	$HCl^* + Cl_2$	S2α	0.5	41.6	31.5	520	6.47^c	55.6
5p	$HF^* + F_2$	S2α	0.5	53.8	22.0	348	22.71	116.1

[a] Claimed to be "instantaneous" in gas phase (M. Trautz and F. A. Henglein, *Z. Anorg. Allgem. Chem.*, **110,** 237(1920)) or to have "significant" lifetime at pressures below 100 mm (see footnote *b* (Jost), Table III). [b] Exchange complete in time needed to separate bromine by freezing, but possibility of separation-induced exchange not excluded (F. S. Klein, A. Persky, and R. E. Weston, Jr., *J. Chem. Phys.*, **41,** 1799 (1964)). [c] Experimental rate (Klein, *et al.*[b]) (atomic chain) is 1.3 times that calculated here.

Table VI. Kinetics of Other Symmetrical Hydrogen Halide Reactions

No.	Reactants	Reaction class	E_m, kcal/mole	$^1/_2D_0{}^\circ + E_c$, kcal/mole	T_r, °K	log Q_r	E_{BH}, kcal/mole
6a	$H^*I + H_2$	S2α	61.8	53.6^a	783	5.28^c	48.4
6b	$H^*Br + H_2$	S2α	68.9	53.6^a	782	7.41^d	53.9
6c	$H^*Cl + H_2$	S2α	76.0	53.6^a	782	9.25^e	57.3
6d	$H^*F + H_2$	S2α	91.6	55.6^b	823	12.31	72.5
6e	$H^*I^* + HI$	S2β	38.3	38.2	*f*	*f*	35.6
6f	$H^*Br^* + HBr$	S2β	52.6	46.2	*f*	*f*	46.9
6g	$H^*Cl^* + HCl$	S2β	66.8	54.1	*f*	*f*	52.9
6h	$H^*F^* + HF$	S2β	98.0	71.0	*f*	*f*	84.1

[a] Calculated for unsymmetrical X–H–H transition state. [b] Calculated for symmetrical H–F–H transition state. [c] Experimental observations (E. J. Rosenbaum and T. R. Hogness, *J. Chem. Phys.*, **2,** 267 (1934)) interpreted (H. Steiner, *Trans. Faraday Soc.*, **36,** 1111 (1940)) to indicate a bimolecular mechanism, but reinterpretation (J. H. Sullivan, *J. Chem. Phys.*, **30,** 1577 (1959)) with new data (Sullivan, Table II, footnote *b*) indicated chain mechanism only and $E_m > 47$ kcal/mole. [d] Experimental rate (H. Steiner, *Proc. Roy. Soc.* (London), **A163,** 531 (1939)) (atomic chain) is four times that calculated here. [e] Experiments (P. Gross and H. Steiner, *J. Chem. Phys.*, **4,** 165 (1936); H. Steiner and E. K. Rideal, *Proc. Roy. Soc.* (London), **A173,** 503 (1939)) interpreted (Steiner and Rideal) to indicate most of reaction by atomic chain mechanism at rate 1.6 times that calculated here. Additional contribution from bimolecular mechanism with E_m of 55 kcal/mole is also claimed (Steiner and Rideal). Potential experimental difficulties do not justify calculations.

oxygen represent exceptions because of multiple bonding possibilities for first row elements.

However, these elements can also form quite stable species like CO_2, N_2O, NO_2, H_2O, and HO_2 that permit reaction by paths excluded from consideration in these papers.

Table VIII contains calculations based on the assumption that no stable or metastable species contains more than two atoms. The footnotes suggest more complex mechanistic pathways for reactions of these multivalent elements.

Table VII. Kinetics of Reactions Involving Alkalies

No.	Reactants	Reaction class	$\chi^\ddagger$	E_m, kcal/mole	$^1/_2D_0{}^\circ + E_c$, kcal/mole
7a	$Na_2 + Cl_2$	U2α	0.088	1.1	8.6^a
7b	$2NaH$	U2β	0.416	27.1^b	47.0^c
7c	$Na_2 + HCl$	U3α	0.440	33.1	14.8
7d	$NaH + Cl_2$	U3α	0.221	9.3	23.5
7e	$NaH + HCl$	U3β	0.399	38.5	25.5
7f	$Na_2 + Na^*Cl$	S2α	0.5	37.8	11.6
7g	$Cl_2 + NaCl^*$	S2α	0.5	41.0	31.5
7h	$NaCl + Na^*Cl^*$	S2β	0.5	65.5^d	52.0
7i	$Na_2 + Na^*H$	S2α	0.5	22.2	11.6
7j	$H_2 + NaH^*$	S2α	0.5	59.7	53.6
7k	$NaH + Na^*H^*$	S2β	0.5	34.2	26.5

[a] Shown (M. Polanyi and G. Schay, *Z. Physik. Chem.*, **B1,** 30 (1928)) to be very fast atomic chain under conditions where Na_2 molecules in very low concentration relative to Na atoms. [b] Reaction takes place in condensed phase by undertermined mechanism with activation energy (C. C. Addison, R. J. Pulham, and R. J. Roy, *J. Chem. Soc.*, 4895 (1964)) of 24.9 kcal/mole. [c] Initial rate for atomic nonchain mechanism.[1] Once elemental sodium was present, the activation energy would drop to 41.3 kcal/mole. [d] NaCl vapor contains significant concentration of dimers (S. A. Ochs, R. E. Coté, and P. Kusch, *J. Chem. Phys.* **21,** 459 (1953)). If they are symmetrical and in rapid equilibrium, this value of E_m is much too high.

Discussion

Comparison with Experiment. The calculations include bimolecular activation energies for 110 different possible reactions of molecules involving 11 different elements. Of these reactions, 47 lead to net chemical reaction and 63 are symmetrical. To the extent they could be isolated from complications under conditions appropriate for study, 64 are predicted to go by bimolecular mechanisms and 46 by atomic chain or atomic nonchain mechanisms. It appears to be an historical accident that so few bimolecular mechanisms have been clearly established previously.

Only ten of these reactions have been subjected to reasonably careful kinetic study in gas phase. Seven of these—the atomic scrambling of hydrogen (1a), the

Table VIII. Kinetics of Reactions Involving Carbon, Nitrogen, and Oxygen

No.	Reactants	Reaction class	$x^{\ddagger}$	E_m, kcal/mole	$^1/_2D_0{}^\circ + E_c$, kcal/mole	T_r, °K	log Q_r
8a	2NO	U2β	0.424	54.0[a]	127.0[b]	1220	−9.67[c]
8b	N_2 + N*O	S2α	0.5	88.8[d]	114.5	1830	−0.18
8c	O_2 + NO*	S2α	0.5	59.0[e]	63.0	1052	2.43
8d	NO + N*O*	S2β	0.5	66.7[f]	79.0	1320	1.75[g]
8e	O_2 + CO*	S2α	0.5	99.9[h]	63.0	1010	11.34
8f	CO + C*O*	S2β	0.5	148.6[i]	129.9	2110	5.37
8g	H_2 + O_2	U2α	0.536	77.9[j]	*k*	*k*	*k*

[a] Experimental values are 63.8 kcal/mole (F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, **23**, 1702 (1955)) and 63.1 kcal/mole (E. L. Yuan, J. I. Slaughter, W. E. Koerner, and F. Daniels, *J. Phys. Chem.*, **63**, 952 (1959)). However, endothermic formation of N_2O + O (ΔH° = 35.45 kcal/mole) offers alternative mechanism with same kinetics. [b] Computed for initial rate. As product oxygen is formed, the apparent activation energy will drop to 105.0 kcal/mole. [c] Second-order kinetics at about predicted rate are observed in this temperature range (Kaufman and Kelso, and Yuan, *et al.*, footnote *a*), but the mechanism is not necessarily bimolecular (see footnote *a*). Atomic chain mechanisms become dominant at high temperatures in shock waves (H. S. Glick, J. J. Klein, and W. Squire, *J. Chem. Phys.*, **27**, 850 (1957); R. E. Duff and N. Davidson, *ibid.*, **31**, 1018 (1959)) as predicted in the first paper of this series.[1] [d] Endothermic formation of N_2O + N (ΔH° = 110.4 kcal/mole) offers implausible alternative mechanism with same kinetics. [e] Endothermic formation of NO_2 + O (ΔH° = 45.65 kcal/mole) offers alternative mechanism with same kinetics. [f] Unlikely to compete with reactions leading to process 8a. [g] Claimed to be rapid at room temperature (W. Spindel and M. J. Stern, *ibid.*, **32**, 1579 (1960)) but the possibility of catalysis by higher oxides of nitrogen is not excluded. [h] Exothermic formation of CO_2 + O (ΔH° = −8.48 kcal/mole) would complicate the system. [i] Endothermic formation of CO_2 + C (ΔH° = 130.48 kcal/mole) could complicate the system. [j] Claimed (D. L. Ripley and W. C. Gardiner, Jr., *ibid.*, **44**, 2285 (1966)) to have an activation energy about 39 kcal/mole. Endothermic formation of HO_2 + H (ΔH° = 58 kcal/mole) and H_2O + O (ΔH° = 1.4 kcal/mole) could complicate the system. [k] Additional complications do not justify calculations.

syntheses of hydrogen bromide (2b) and hydrogen chloride (2c), the exchange of hydrogen chloride with chlorine (5o), and the exchanges of hydrogen with hydrogen iodide (6a), hydrogen bromide (6b), and hydrogen chloride (6c)—proceed by atomic chain mechanisms as predicted. Calculated and observed rates agree to better than a factor of two for four of the six independent cases, while the disagreement in one case is slightly more than an order of magnitude. Calculation and experiment also agree in predicting bimolecular mechanisms for hydrogen iodide synthesis (2a) and nitric oxide decomposition (8a), although the rate-determining step in the latter reaction may produce an atom and a triatomic molecule instead of two diatomic molecules as assumed. For one of these most studied reactions—reaction of hydrogen with iodine chloride (2f)—a bimolecular mechanism at variance with the calculations is claimed,[5] but reasons have been given for disputing the claim. Additional bimolecular contributions to the rate have also been claimed for the exchange of hydrogen with hydrogen iodide[8] (6a) and with hydrogen chloride[9] (6c), but these claims are questioned above (6c) or already disproved[10] (6a).

Ten additional reactions have been studied less thoroughly or by methods giving less absolute values for rate constants. For six of these reactions—reactions of hydrogen with fluorine (2d) and with iodine bromide (2e), syntheses of iodine bromide (3a), bromine chloride (3c), and sodium chloride (7a), and decomposition of sodium hydride (7b)—available evidence is consistent with the calculations. For four other reactions—reactions of hydrogen bromide with chlorine (5c) and with bromine (5n) and self-exchange of sodium chloride (7h) and nitric oxide (8d)—some evidence suggests very rapid equilibration under conditions where the calculations predict much slower reaction. Although the Cl_2 + HBr observations (5e) are hard to explain except as a discrepancy with calculations, the other cases involve either equivocal interpretations or molecules with atoms having unfilled valence shells.

This summary indicates a generally encouraging correlation of calculation with experiment for a wide range of reaction types, but much more experimental information is needed. It is inconceivable that the literature survey for this comparison has been complete. If any reader knows of additional experimental work that has been overlooked, that information would be greatly appreciated.

Comparison with Benson and Haugen.[2] Activation energies for bimolecular mechanisms for 37 of the same reactions were calculated independently by a very different method by Benson and Haugen.[2] Their activation energies are higher than those reported here except for symmetrical transition states containing two or more atoms of hydrogen. Their estimates are particularly high for reactions involving elementary fluorine, and sometimes differ from those of this paper by over 90 kcal/mole!

Since the two computational methods give clearly different predictions, experimental measurements should permit at least one of these methods to be unequivocally rejected.

Factors Affecting Activation Energies. Values of E_m in the above tables suggest a few factors that influence activation energies for four-center reactions. **Bond energy** has long been recognized as one of those factors, and molecules with strong bonds require higher activation energies for reaction.

Exothermicity of the reaction is another factor tending to lower activation energy. The method of computation automatically introduces a contribution for this effect, and values of $x^{\ddagger}$ deviate more from 0.5 as reactions become more exothermic. This effect is in complete agreement with the postulate of Hammond[11] about similarity of reactants and transition states for exothermic reactions.

Polarizability has been less clearly recognized as a factor influencing activation energy, although Franck

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(8) H. Steiner, Table VI, footnote *c*.
(9) H. Steiner and E. K. Rideal, Table VI, footnote *e*.
(10) J. H. Sullivan, Table VI, footnote *c*.

(11) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

and Rabinowitch[12] pointed out that the ratio of collision diameter to internuclear distance was much less for halogens than for oxygen and nitrogen. They inferred that halogens should form four-center transition states particularly easily; subsequent political events may have interfered with more quantiative development of the idea. Isotopic scrambling (Sl) reactions illustrate the effect with E_m/D_e values ranging from 0.778 for hydrogen to 0.187 for iodine.

The computational method employed recognizes contributions from all three of these factors, but it would be fortuitous if it properly balances their magnitudes. Much more experimental information will be needed before relative contributions can be assigned with any confidence.

Factors Neglected in Calculations. The computational method for estimating E_m also neglects several factors that undoubtedly contribute. **Zero-point energy** is such a factor. A more sophisticated treatment could have started from energy $-D_0°$ instead of $-D_e$ and recognized the existence of zero-point energy effects in the transition state. Few if any computed activation energies would have been shifted more than 2 or 3 kcal/mole by the more involved procedure. Zero-point energies should not be introduced unless experimental work indicates these calculations are more reliable than there is any reason to hope.

Isotope effects have also been neglected. Excellent procedures already exist for treating change of nuclear mass as a perturbation on a reaction of known characteristics. There is no reason to introduce them into the present calculations which presuppose much less initial knowledge about the system.

Dipole–dipole interactions, which are made the basis of the Benson–Haugen[2] method, are completely neglected. Such interactions are of the order of μ^2/s^3 where μ is the dipole moment of one side of a four-center transition state and s is the separation of the centers of opposite sides. The magnitude of this quantity was estimated for transition states for the formation of hydrogen chloride (2c) and sodium chloride (7a) with the assumption that dipole moments of opposite sides were the same as those of the final molecules. Both calculations added 2.0 kcal/mole to the calculated activation energy, and the effect would be smaller in most other reactions in the tables. Such a refinement is not yet justified.

Except for multiplicity contributions to entropies, the calculations have neglected possible influences of **electronic configuration.** Possible dangers of this neglect are suggested by the observation[13] that the activation energy is virtually zero for the second-order reaction of 2ClO with eventual formation of $Cl_2 + O_2$. The method proposed here would certainly predict a very appreciable activation energy if this reaction does involve a four-center transition state. However, Benson and co-workers[14,15] have suggested that the initial and rate-determining step is the thermoneutral formation of ClOO + Cl. Hence this reaction resembles those others in Table VIII that may proceed through triatomic molecule intermediates. It may also be that this method of estimating activation energies must be restricted to elements like hydrogen and the halogens for which all s and p orbitals of the same principal quantum number are either filled with electron pairs or used in σ bonding. Such a restriction would remove any need for concern that the calculations fail to predict the apparent rapid double exchanges of sodium chloride (7h) and nitric oxide (8d).

Suggestions for Future Work. Rates of reaction by atomic chain mechanisms can obviously be predicted with considerable confidence. The great need is for experimental studies of reactions proceeding by bimolecular mechanisms. Even if such studies undermine the validity of both the present method and that of Benson and Haugen,[2] the data will be needed for testing the successful theory that must ultimately develop.

This paper suggests the desirability of careful observation of more systems than the author has opportunity or inclination to undertake in his laboratories. Work presently under way at the University of Oregon is being concentrated on halogen–halogen and halogen–hydrogen halide reactions, and it will by no means exhaust these categories. If persons intending to study any reactions of diatomic molecules will notify the author of the systems they propose to examine, he will be happy to act as a clearing house to get them in contact with other persons studying related systems so that duplication of effort can be avoided.

Acknowledgment. Initial work on this problem at the University of Oregon was supported in part by a grant from the U. S. Army Research Office. The activation energies were calculated at the Victoria University of Wellington during tenure of a Fulbright award. The final calculations of T_r and the preparation of the initial manuscript were completed at the Max-Planck-Institut during tenure of a National Science Foundation Senior Postdoctoral Fellowship.

Dr. F. S. Klein of the Weizmann Institute in Rehovoth, Israel suggested useful references. Drs. H. S. Johnston, S. W. Benson, and S. H. Bauer revealed their identities as referees and made many suggestions that greatly aided an extensive revision of the original manuscript. They share no responsibility for any faults in what has finally emerged.

Appendix I. Assumptions Used in Entropy Calculations

Three-Atom Transition States. Every three-atom transition state was assumed to be linear. The symmetry number was always set equal to unity; this formalism automatically takes care of the correction discussed by Bishop and Laidler.[16]

The moment of rotational inertia was computed assuming equilibrium internuclear distances between adjacent atoms, and the resulting value was multiplied by two; this stretches bonds about 40% in the transition state.

The electronic entropy was set equal to $R \ln (2S + 1)$ where S is the minimum electronic spin obtainable by combining ground states of the reactant atom and molecule. Except for reactions of C, N, and O, the value was always $R \ln 2$.

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(12) J. Franck and E. Rabinowitch, *Z. Elektrochem.*, **36**, 794 (1930).

(13) G. Porter and F. J. Wright, *Discussions Faraday Soc.*, **14**, 23 (1953).

(14) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **27**, 1382 (1957).

(15) S. W. Benson and K. H. Anderson, *ibid.*, **31**, 1082 (1959).

(16) D. M. Bishop and K. J. Laidler, *ibid.*, **42**, 1688 (1965).

Vibrational contributions to entropy were neglected both for the reactant diatomic molecule and for the transition state. This decision was taken because the known preexponential term for the reaction of Br + H_2 could be fitted well by the other assumptions without any consideration of vibration. This transition state is particularly "stiff," and vibrational entropy is probably more significant in some of the other reactions. Inclusion of vibration would increase the importance of the atomic chain mechanism for some reactions of halogen molecules but would not significantly affect the mechanistic conclusions.

Four-Atom Transition States. Every four-atom transition state was assumed to be planar. By employing the following symmetry numbers, the correction of Bishop and Laidler[16] was formally taken care of. For A_4 transition states, the symmetry number was four and the rate was written as $k[A_2]^2$. For A_2B_2 transition states, the symmetry number of two was used regardless of whether atoms of the same element were on opposite or adjacent corners. Symmetry numbers for all other transition states were assumed to be unity.

Transition states with formula A_4 were assumed to be square. Those with formula A_3B had AB and AA diagonals with lengths in the same ratio as the bond lengths of those molecules. Those with formulas A_2B_2 and like atoms on opposite corners were rhombohedral with diagonals in the ratio of AA and BB bond lengths; those with like atoms on adjacent corners had AA and BB sides parallel. For other transition states, the longest side and the one opposite were assumed to be parallel. For each transition state, moments of inertia were computed with the lengths of the sides equal to appropriate molecular internuclear distances, and the value of $(I_aI_bI_c)^{1/2}$ so obtained was multiplied by a factor of three to take care of bond expansion during formation of the transition state.

Electronic entropies were assumed to be zero for all transition states except those that could be formed from oxygen or nitric oxide; these had the minimum values to be expected from multiplicities if no electron spins were reversed.

Four of the five vibration frequencies of the transition state were each set equal to 0.40 times the frequency of the diatomic molecule appropriate to one of the four sides, and the fifth frequency was set equal to twice the minimum of the other four frequencies. Entropy contributions were then calculated. This treatment gave a fair fit to the observed entropy of activation for the reaction of hydrogen and iodine and a rather poor fit for nitric oxide decomposition. The method is certainly very crude but can be applied easily to a large number of reactions.

Reactions of Diatomic Molecules. III. Kinetics of Formation of Iodine Bromide

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Received March 1, 1966

Abstract: Iodine and bromine in carbon tetrachloride at 26.3° react by a bimolecular mechanism with rate constant of 510 l./mole sec. This is the first quantitative kinetic study of a halogen–halogen reaction, and the result is in good agreement with recent calculations indicating that such reactions should proceed by bimolecular mechanisms.

It has been predicted[1] that all reactions of halogens with halogens will take place by bimolecular rather than atomic chain mechanisms. No such reaction has received a detailed kinetic study.

The reaction of iodine with bromine to form IBr was selected for preliminary study because it was predicted[1] to be among the most rapid of the halogen–halogen reactions. This prediction was supported by qualitative observations of carbon tetrachloride solutions by Forbess and Schoonover at the University of Oregon and by a single stopped-flow measurement by Sturtevant at Yale University. In this paper, we report more extensive stopped-flow measurements in the same solvent.

Experimental Section

Reagent grade iodine was further purified by slow sublimation. Reagent grade bromine was shaken with concentrated sulfuric acid and distilled. The solvent was reagent grade carbon tetrachloride that had been distilled three times from phosphorus pentoxide.

Solutions of the halogens were analyzed spectrophotometrically with the use of the extinction coefficients reported by Tilich.[2]

The stopped-flow apparatus was based on the designs of Gibson[3] and Sutin.[4] Solutions came in contact only with glass and Teflon. The transmittance of the reaction mixture was monitored during reaction by a photomultiplier tube receiving light of 5400 A provided by the light source and monochromater of a Beckman DU spectrophotometer. The output from the photomultiplier was then put on a Tektronix 561A oscilloscope and the trace was photographed. The temperature of the room was kept at 26.3° during the runs.

Results

Let k be the rate constant in the forward direction for the bimolecular reaction

$$I_2 + Br_2 \longrightarrow 2IBr \qquad (1)$$

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[1] R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4318 (1966).

[2] L. S. Tilich, *J. Gen. Chem. USSR*, **22**, 795 (1952).

[3] Q. H. Gibson, *Discussions Faraday Soc.*, **17**, 137 (1954).

[4] N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).