JOURNAL OF CATALYSIS 8, 137-144 (1967)

Kinetic Structural Analysis of Catalytic Disproportionation of Freons

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Received November 1, 1966; revised February 7, 1967

Assuming for the catalytic disproportionation of $CHCl_2F$ on a highly fluorinated alumina a mechanism involving interactions of each chemical species (reagents and products) with the catalyst, the reacting system should appear to be pseudomonomolecular. The reaction has been investigated by methods of kinetic structural analysis developed by Wei and Prater for these systems. Results of treatment were found to be consistent with experimental kinetic data. A sequence of halogen exchange intermediate reactions between reagents and catalyst has been postulated to explain the pseudo-first-order kinetics of the disproportionation reactions.

INTRODUCTION

In a largely comprehensive paper, Wei and Prater (*1*) outlined concepts and methods of kinetic structural analysis of complex reaction systems. Their treatment was chiefly devoted to a special class of reaction systems, namely monomolecular systems, but pseudomonomolecular systems can be equally treated by the same or a slightly modified procedure. Since many heterogeneous catalytic systems can be reduced to this class of reaction systems, the structural approach becomes suitable for an extensive application. Exact mathematical tools are available for deriving rate parameters from experimental kinetic data only for linear systems, but one can expect that at least approximate tools would be developed in the near future for nonlinear systems.

Wei and Prater reported an application of this method to a three-component system, namely, the butene isomerization over alumina catalyst studied by Haag and Pines (*2*). Xylene isomerization on SiO_2-Al_2O_3 catalysts has been successfully investigated by Silvestri and Prater by methods of structural kinetic analysis (*3*). In this work we tried to extend the method to a particular four-component system, the catalytic disproportionation of chlorofluoromethanes, with the stimulating perspective that this system could be reduced to a special pseudomonomolecular system by some mechanistic hypotheses.

The aims of our work were essentially two: first, to define the structural features of this peculiar system by application of the Wei-Prater treatment, second to test the soundness of the proposed mechanism on the basis of consistency of results of this treatment with experimental kinetic data. For fundamentals of the method and for terminology and symbols of the procedure reference must be made to the basic work of Wei and Prater (*1*).

2. EXPERIMENTAL

$CHCl_2F$ supplied by I.C.I. (trade name Arcton 21) was used as reactant for disproportionation reactions without further purification. The catalyst has been prepared by vapor-phase fluorination of catalytic alumina supplied by Alcoa (trade name Alumina F-1) with hydrogen fluoride at 400°C. The final content of fluorine in the catalyst was 53%. $CHCl_2F$ flowed through a rotameter to a small glass reactor filled with 2.5 g of catalyst. Constant temperature along the reactor was assured by a silica fluid bed thermostated within ±2°C.

TABLE 1

EXPERIMENTAL COMPOSITION POINTS FOR DISPROPORTIONATION REACTION OF PURE $CHCl_2F$ AT 200°C

Runs[a]	Reaction products (mole fractions)				Halogen balances (moles)	
	$CHCl_2F$	$CHClF_2$	CHF_3	$CHCl_3$	Cl	F
1	0.850	0.063	0.002	0.085	2.028	0.982
2	0.780	0.106	0.004	0.110	1.996	1.004
3	0.435	0.239	0.035	0.291	1.982	1.018
4	0.378	0.255	0.036	0.331	2.004	0.996
5	0.318	0.268	0.047	0.367	2.005	0.995
6	0.289	0.277	0.055	0.379	1.992	1.008
7	0.225	0.286	0.072	0.417	1.987	1.013
8	0.201	0.286	0.078	0.435	1.993	1.007
9	0.176	0.262	0.078	0.484	2.066	0.934
10	0.086	0.215	0.172	0.527	1.968	1.032
11	0.050	0.120	0.235	0.595	2.005	0.995

[a] At different contact times.

Reaction products were sent to a soda-lime trap to eliminate the small quantities of cracking products formed at highest conversions and then to a sampling four-way valve. At any rate, samples of reaction products can be injected into a chromatographic unit equipped with 2 m of a type A Perkin-Elmer column (diisodecylphthalate on Celite GC 22) operated at 70°C with helium as carrier gas. All the connecting tubes and sampling valves were thermostated at 70°C to avoid condensation of high-boiling products. Table 1 shows conditions and results of catalytic runs. Compositions of reaction products are expressed as mole fractions. The unbalancing in fluorine and chlorine indicates that the disproportionation reaction is accompanied by some cracking of reaction products: this fact is confirmed by coke formation on the catalyst during the reaction and by acidic vapors adsorbed in the soda lime trap.

3. MECHANISM HYPOTHESIS

Stoichiometrically, our system can be described by the reactions

$$\begin{aligned} 2CHCl_2F &= CHClF_2 + CHCl_3 \\ 2CHClF_2 &= CHF_3 + CHCl_2F \end{aligned} \qquad (1)$$

We started from the hypothesis that catalytic disproportionation could be represented by a sequence of intermediate steps involving interaction of each chemical species with catalyst; this interaction could be a halogen exchange reaction. Let us indicate

$A_1 = CHCl_2F$
$A_2 = CHClF_2$
$A_3 = CHF_3$
$A_4 = CHCl_3$

and

U_0, fluorinating active center of catalyst
U_1, chlorinating active center of catalyst

Thus the sequence of steps may be represented by the following basic equations:

$$A_1 + U_0 \rightleftharpoons A_2 + U_1 \qquad (2a)$$

$$A_1 + U_1 \rightleftharpoons A_4 + U_0 \qquad (2b)$$

$$A_2 + U_0 \rightleftharpoons A_3 + U_1 \qquad (2c)$$

In order to account for the experimentally obtained completeness of disproportionation reactions of $CHCl_2F$ or $CHClF_2$ to $CHCl_3$ and CHF_3, the rate constants of formation of these products must be very much higher than the rate constants of disappearance, allowing for neglect of the backward reactions (2b) and (2c):

$$\begin{aligned} A_1 + U_0 &\underset{k'_{12}}{\overset{k'_{21}}{\rightleftharpoons}} A_2 + U_1 \\ A_1 + U_1 &\xrightarrow{k'_{41}} A_4 + U_0 \\ A_2 + U_0 &\xrightarrow{k'_{32}} A_3 + U_1 \end{aligned} \qquad (3)$$

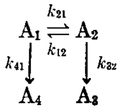
where k'_{ij} indicate rate constants of reactions converting A_j into A_i. The rate of change of each chemical species in scheme (3) is given by

$$\begin{aligned} da_1/dt &= -k'_{21}u_0a_1 - k'_{41}u_1a_1 + k'_{12}u_1a_2 \\ da_2/dt &= k'_{21}u_0a_1 - k'_{32}u_0a_2 - k'_{12}u_1a_2 \\ da_3/dt &= k'_{32}u_0a_2 \\ da_4/dt &= k'_{41}u_1a_1 \end{aligned} \qquad (4)$$

where a_i indicate concentrations of chemical species A_i and u_i concentrations of active centers U_i. At the steady state, u_i must be constant then Eq. (4) can be written as follows:

$$\begin{aligned} da_1/dt &= -(k_{21} + k_{41})a_1 + k_{12}a_2 \\ da_2/dt &= k_{21}a_1 - (k_{32} + k_{12})a_2 \\ da_3/dt &= k_{32}a_2 \\ da_4/dt &= k_{41}a_1 \end{aligned} \qquad (5)$$

where k_{ij} is now the pseudo-first-order rate constant of the reaction converting A_j into A_i species. These equations are representative of an irreversible pseudomonomolecular system



$$\begin{tikzcd} A_1 \arrow[r, shift left, "k_{21}"] \arrow[d, "k_{41}"'] & A_2 \arrow[l, shift left, "k_{12}"] \arrow[d, "k_{32}"] \\ A_4 & A_3 \end{tikzcd} \qquad (6)$$

In this final arrangement the reaction system is ready to be submitted to the structural treatment; the results of this treatment will be compared with the experimental kinetic data.

4. Structural Treatment

The equation system (5) can be written in the form of matrices

$$d\boldsymbol{\alpha}/dt = \mathbf{K}\boldsymbol{\alpha}$$

where

$$\boldsymbol{\alpha} = \begin{vmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{vmatrix}, \quad \frac{d\boldsymbol{\alpha}}{dt} = \begin{vmatrix} da_1/dt \\ da_2/dt \\ da_3/dt \\ da_4/dt \end{vmatrix}$$

$$\mathbf{K} = \begin{vmatrix} -(k_{21} + k_{41}) & k_{12} & 0 & 0 \\ k_{21} & -(k_{32} + k_{12}) & 0 & 0 \\ 0 & k_{32} & 0 & 0 \\ k_{41} & 0 & 0 & 0 \end{vmatrix} \qquad (7)$$

Since our system is a four-component system, the problem is to find four characteristic compositions obeying the conditions

$$\mathbf{K}\boldsymbol{\alpha}_j^+ = -\lambda_j \boldsymbol{\alpha}_j^+ \qquad j = 0, 1, 2, 3 \quad (8)$$

or

$$\mathbf{K}\mathbf{x}_j = -\lambda_j \mathbf{x}_j$$

where λ_j is a scalar constant.

At equilibrium it is required that at least one of the eigenvalues λ_j has to be zero: the related eigenvector represents the equilibrium composition of the system. Furthermore, all the mass of the system must be accounted for by the eigenvector with $\lambda_j = 0$. If one expresses A_i concentrations as mole fractions, any linear combination of vectors

$$\begin{vmatrix} 0 \\ 0 \\ 1 \\ 0 \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} 0 \\ 0 \\ 0 \\ 1 \end{vmatrix}$$

is a characteristic vector with $\lambda = 0$. Since our experimental data have been obtained from pure A_1, equilibrium composition will be

$$\mathbf{x}_0 = \begin{vmatrix} 0 \\ 0 \\ 0.333 \\ 0.667 \end{vmatrix}$$

Owing to degeneracy in $\lambda = 0$ of our system, another characteristic vector can be chosen among the vectors defined by linear combination of

$$\begin{vmatrix} 0 \\ 0 \\ 1 \\ 0 \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} 0 \\ 0 \\ 0 \\ 1 \end{vmatrix}$$

For sake of simplicity in calculations, this vector has been chosen as

$$\mathbf{x}_1 = \begin{vmatrix} 0 \\ 0 \\ 0 \\ 1 \end{vmatrix}$$

Two other characteristic vectors, with $\lambda \neq 0$, are now to be found: the first one can be derived from experimental data plotted in Fig. 1 by the extrapolation procedure described by Wei and Prater (*1*)

$$\boldsymbol{\alpha}_{\mathbf{x}_2}(0) = \begin{vmatrix} 0.170 \\ 0.415 \\ 0.000 \\ 0.415 \end{vmatrix} \quad \text{and } \mathbf{x}_2 = \begin{vmatrix} 0.170 \\ 0.415 \\ -0.333 \\ -0.252 \end{vmatrix}$$

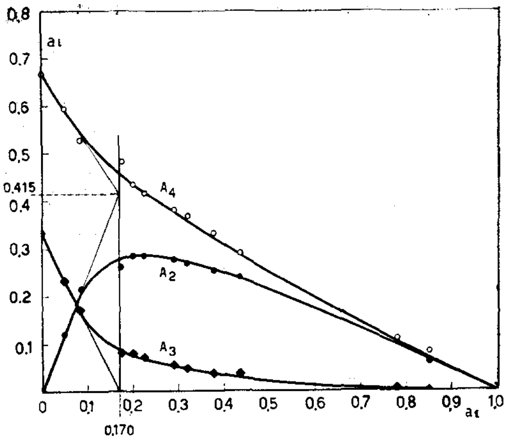


FIG. 1. Experimental compositions for catalytic disproportionation of pure $CHCl_2F$ at 200°C. $A_1 = CHCl_2F$; $A_2 = CHClF_2$; $A_3 = CHF_3$; $A_4 = CHCl_3$; a_i = mole fraction of A_i.

Substituting in Eq. (8) and solving, one obtains the ratios between the pseudo-first-order rate constants

$$\frac{k_{12}}{k_{21}} = 0.545 \quad \frac{k_{32}}{k_{21}} = 0.545 \quad \frac{k_{41}}{k_{21}} = 0.994$$

i.e., for $k_{21} = 1$, the values of the relative rate constants. Hereinafter, we will indicate them with the identical symbols k_{ij}. Here it must be pointed out that the close values of relative constants k_{12} with k_{32} and k_{41} with k_{21} mean that halogen exchange reactions are well balanced within each of the two disproportionation reactions (1) according to reaction stoichiometry.

At this point we can construct the relative rate constants matrix **K**

$$\mathbf{K} = \begin{vmatrix} -1.994 & 0.545 & 0 & 0 \\ 1 & -1.090 & 0 & 0 \\ 0 & 0.545 & 0 & 0 \\ 0.994 & 0 & 0 & 0 \end{vmatrix} \tag{9}$$

The last problem is to define the fourth unit characteristic vector. In order to derive it, use can be made of orthogonality relations between characteristic vectors. The first two elements of each characteristic vector must be always consistent with the subreaction

$$A_1 \underset{k_{12}}{\overset{k_{21}}{\rightleftharpoons}} A_2 \tag{10}$$

If we indicate equilibrium composition of A_1 and A_2 by a_1^* and a_2^*, respectively, the following conditions must be satisfied

$$k_{21}a_1^* = k_{12}a_2^*; \qquad a_1^* + a_2^* = 1$$

By application to $\mathbf{x}_2$ of orthogonality transformation matrices $\mathbf{D}^{-\frac{1}{2}}$ and $\mathbf{D}^{\frac{1}{2}}$, derived from a_1^* and a_2^* and the equation of constraints of the system given in the case of equilibrium point $a_3^* = 0.333$ and $a_4^* = 0.667$ by equations

$$a_1 + 2a_2 + 3a_3 = 1 \quad a_1 + a_2 + a_3 + a_4 = 1 \tag{11}$$

we have

$$\boldsymbol{\alpha}_{\mathbf{x}_3}(0) = \begin{vmatrix} -1.985 \\ 1.491 \\ 0.000 \\ 1.494 \end{vmatrix} \qquad \mathbf{x}_3 = \begin{vmatrix} -1.985 \\ 1.491 \\ 0.333 \\ 0.827 \end{vmatrix}$$

By these unit characteristic vectors, the transformation matrix **X** can be constructed and inverse matrix $\mathbf{X}^{-1}$ derived.

At this point the original system of chemical species A_i can be completely decoupled by transforming compositions $\boldsymbol{\alpha}$ of A_i system into compositions $\boldsymbol{\beta}$ of a new system of hypothetical species B_i by means of transformation matrix $\mathbf{X}^{-1}$

$$\mathbf{X}^{-1}\boldsymbol{\alpha}(t) = \boldsymbol{\beta}(t) = \begin{vmatrix} b_0(t) \\ b_1(t) \\ b_2(t) \\ b_3(t) \end{vmatrix} \tag{12}$$

By using some experimental A compositions taken from Table 1, one obtains the B compositions of Table 2. From Table 2 it can be seen that among the hypothetical species of the B system, B_0 does not react and contains all the mass of system, B_1 is always zero and B_2 and B_3 decay to zero along the reaction path to equilibrium. Kinetic equations of the new hypothetical system can be written, in matrix notation, as

$$d\boldsymbol{\beta}/dt = \boldsymbol{\Lambda\beta} \tag{13}$$

where $\boldsymbol{\Lambda}$ is a diagonal matrix whose elements λ_0, λ_1, λ_2, and λ_3 are the eigenvalues of the unit characteristic vectors in the A system.

The values of λ_0 and λ_1 have been found to be zero. The ratio λ_2/λ_3 can be obtained from the slope of straight line $\ln b_2$ vs. $\ln b_3$

TABLE 2

CORRESPONDING COMPOSITION POINTS IN A AND B SYSTEMS

$\alpha(0) = \begin{vmatrix} 1 \\ 0 \\ 0 \\ 0 \end{vmatrix}$	$\beta(0) = \begin{vmatrix} 1.000 \\ -0.007 \\ 1.384 \\ -0.384 \end{vmatrix}$
$\alpha(t_1) = \begin{vmatrix} 0.770 \\ 0.105 \\ 0.005 \\ 0.115 \end{vmatrix}$	$\beta(t_1) = \begin{vmatrix} 0.995 \\ 0.004 \\ 1.259 \\ -0.279 \end{vmatrix}$
$\alpha(t_2) = \begin{vmatrix} 0.435 \\ 0.240 \\ 0.030 \\ 0.295 \end{vmatrix}$	$\beta(t_2) = \begin{vmatrix} 1.005 \\ -0.008 \\ 1.045 \\ -0.139 \end{vmatrix}$
$\alpha(t_3) = \begin{vmatrix} 0.325 \\ 0.270 \\ 0.045 \\ 0.365 \end{vmatrix}$	$\beta(t_3) = \begin{vmatrix} 1.000 \\ 0.002 \\ 0.948 \\ -0.082 \end{vmatrix}$
$\alpha(t_4) = \begin{vmatrix} 0.200 \\ 0.285 \\ 0.078 \\ 0.435 \end{vmatrix}$	$\beta(t_4) = \begin{vmatrix} 1.006 \\ -0.007 \\ 0.804 \\ 0.032 \end{vmatrix}$
$\alpha(t_5) = \begin{vmatrix} 0.180 \\ 0.270 \\ 0.090 \\ 0.460 \end{vmatrix}$	$\beta(t_5) = \begin{vmatrix} 0.990 \\ 0.009 \\ 0.747 \\ -0.026 \end{vmatrix}$

drawn in Fig. 2, from data tabulated in Table 2.

Since we know **X**, $\mathbf{X}^{-1}$, and $\mathbf{\Lambda}'$ (putting $\lambda_2 = 1$) rate constant matrix $\mathbf{K}'$ for the A system can be derived from the relation

$$\mathbf{K}' = \mathbf{X} \cdot \mathbf{\Lambda}' \cdot \mathbf{X}^{-1} \tag{14}$$

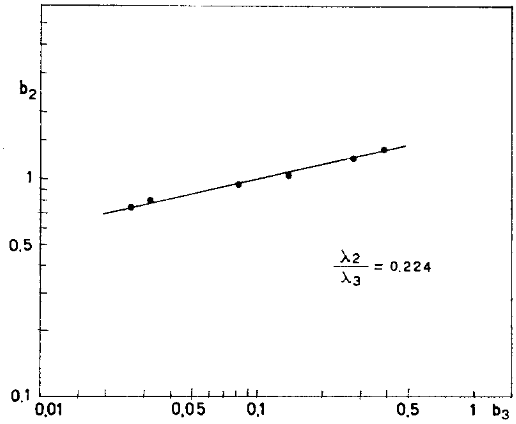


FIG. 2. Determination of λ ratios from graph of $\ln b_2$ vs. $\ln b_3$.

Solving and normalizing k_{21}, one obtains the relative rate constant matrix:

$$\mathbf{K} = \begin{vmatrix} -1.880 & 0.547 & 0 & 0 \\ 1 & -0.915 & 0 & 0 \\ -0.055 & 0.429 & 0 & 0 \\ 0.890 & -0.060 & 0 & 0 \end{vmatrix} \tag{15}$$

In the experimental part we pointed out that the actual reaction is slightly impure with respect to scheme (1). This fact can

TABLE 3

CALCULATED COMPOSITION POINTS FOR DISPROPORTIONATION REACTION OF PURE A_1

$\alpha(0) = \begin{vmatrix} 1 \\ 0 \\ 0 \\ 0 \end{vmatrix}$	$\alpha(0.1) = \mathbf{T}^{0.1}\alpha(0)$	$\alpha(0.1) = \begin{vmatrix} 0.700 \\ 0.153 \\ 0.000 \\ 0.147 \end{vmatrix}$
	$\alpha(0.2) = \mathbf{T}^{0.1}\alpha(0.1)$	$\alpha(0.2) = \begin{vmatrix} 0.503 \\ 0.236 \\ 0.011 \\ 0.250 \end{vmatrix}$
	$\alpha(0.3) = \mathbf{T}^{0.1}\alpha(0.2)$	$\alpha(0.3) = \begin{vmatrix} 0.371 \\ 0.276 \\ 0.029 \\ 0.324 \end{vmatrix}$
	$\alpha(0.4) = \mathbf{T}^{0.1}\alpha(0.3)$	$\alpha(0.4) = \begin{vmatrix} 0.282 \\ 0.289 \\ 0.050 \\ 0.378 \end{vmatrix}$
	$\alpha(0.5) = \mathbf{T}^{0.1}\alpha(0.4)$	$\alpha(0.5) = \begin{vmatrix} 0.220 \\ 0.290 \\ 0.072 \\ 0.420 \end{vmatrix}$
	$\alpha(0.6) = \mathbf{T}^{0.1}\alpha(0.5)$	$\alpha(0.6) = \begin{vmatrix} 0.178 \\ 0.278 \\ 0.094 \\ 0.452 \end{vmatrix}$
	$\alpha(0.7) = \mathbf{T}^{0.1}\alpha(0.6)$	$\alpha(0.7) = \begin{vmatrix} 0.147 \\ 0.262 \\ 0.115 \\ 0.478 \end{vmatrix}$
	$\alpha(0.8) = \mathbf{T}^{0.1}\alpha(0.7)$	$\alpha(0.8) = \begin{vmatrix} 0.125 \\ 0.243 \\ 0.135 \\ 0.499 \end{vmatrix}$
	$\alpha(0.9) = \mathbf{T}^{0.1}\alpha(0.8)$	$\alpha(0.9) = \begin{vmatrix} 0.103 \\ 0.227 \\ 0.153 \\ 0.518 \end{vmatrix}$

account for the differences between corresponding figures in Eqs. (9) and (15) and for some unexpected nonzero values in (15).

The matrices $\mathbf{X}$, $\mathbf{X}^{-1}$, and $\mathbf{\Lambda}'$ can be used to obtain matrix T^t by which the reaction paths of the system have been reconstructed.

Lines of procedure and results have been reported in Table 3.

Experimental and calculated reaction paths are compared in Fig. 3. The agreement is good enough, if not for confirming the accuracy of the derived rate constants values, at least for supporting the proposed reaction kinetics. A better agreement could be obtained by using more than one initial composition and by purging calculations of computational errors.

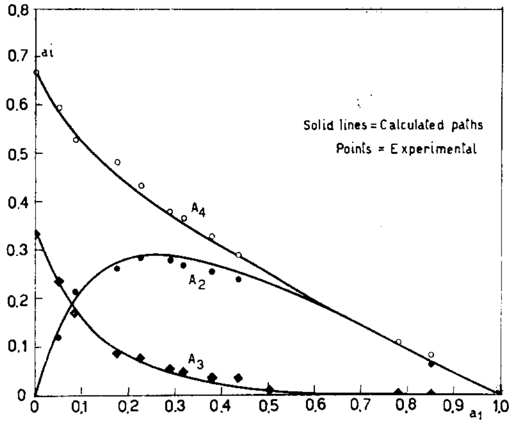


FIG. 3. Comparison of calculated reaction paths with experimental composition for $CHCl_2F$ disproportionation at 200°C.

4. DISCUSSION

The first feature of the system, which emerges from the degeneracy of eigenvectors corresponding to zero eigenvalue, is that it has an infinite number of equilibrium points. This is in agreement with the stoichiometry of the reacting system which evolves to equilibrium compositions between $A_3 = 1$ and $A_4 = 1$ depending on the initial compositions of the reacting mixture.

The aforementioned degeneracy has some implications for the geometrical model of the system: If we regard compositions as vectors, a four-dimensional space with coordinates a_1, a_2, a_3, and a_4 can be used to locate composition vectors of the system at any time. Degeneracy of the system in the zero eigenvalue means that reaction paths must lie on two-dimensional planes contained in this composition space. For our system the general equation for these parallel planes is the equation of constraint

$$a_1 + 2a_2 + 3a_3 = 3a_3^*$$

where the symbols have the usual meaning; it represents a mass balance on F atoms.

Figure 4 shows two of these planes, corresponding to equilibrium compositions $E(0, 0, 0.333, 0.667)$ and $E'(0, 0, 0.667, 0.333)$. For E, displaced characteristic vectors, obtained by moving unit charactersitic vectors along equilibrium composition vector $\mathbf{x}_0$, have been indicated. Displaced characteristic vector $\mathbf{x}_1'$ lies outside of the plane of reaction paths and cannot be used as coordinate axis for the B system. This means that only unit characteristic vectors $\mathbf{x}_0$, $\mathbf{x}_2$, and $\mathbf{x}_3$ completely describe our system. Unit characteristic vector $\mathbf{x}_1$ can perhaps be omitted in calculations; we preferred to include it and obviously we found that the corresponding B_1 species in the B system is always zero in concentration. Unit vector $\mathbf{x}_0$ represents the equilibrium composition, that is, in the B system, the equilibrium species B_0 which does not decay and contains all the mass of the system.

Unit characteristic vector $\mathbf{x}_2$ corresponding to the decaying species B_2 has been derived from the experimental data by the procedure above reported. Figure 4 shows that the same cannot be done for deriving the unit characteristic vector $\mathbf{x}_3$, because displaced characteristic vector $\mathbf{x}_3'$ lies on the plane of reaction paths but outside of the real composition space. This means that the corresponding initial composition $\alpha_{\mathbf{x}_3}(0)$ is not an experimentally realizable composition. Orthogonality relations between characteristic vectors provide means for deriving $\mathbf{x}_3$ and we made use of them.

Consistency of structural features and kinetic behavior of the system with chemical structure and experimental kinetic data strongly suggests that the proposed

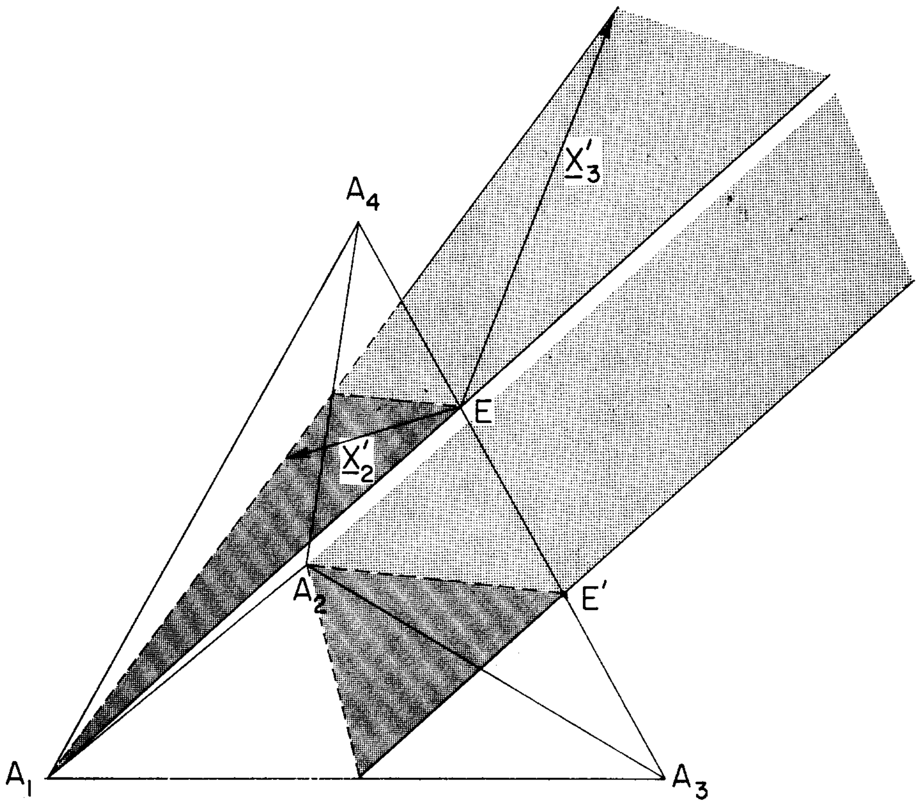


FIG. 4 Subspaces of disproportionation reactions according to scheme (6).

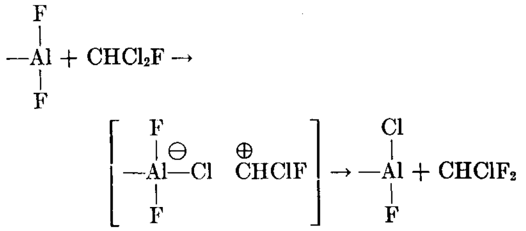
mechanism hypothesis has a very sound basis. In addition, we think that this mechanism could be supported by chemical arguments also.

On the basis of the consideration that our catalyst was a fluorinated alumina, we can suppose that the active centers of reaction are Al halogenides. It is well known that these compounds easily exchange halogen atoms with suitable chemical reagents. Miller (*4*) reported that $AlCl_3$ causes rearrangements as well as replacements of fluorine by chlorine in some unsaturated chlorofluorocarbons. Boggs and co-workers (*5*) showed that hydrogen chloride can exchange its tagged chlorine with chlorofluoromethanes and explained the exchange mechanism by a dissociative adsorption of the organic chlorofluoride on the active surface

Gens (*6*) and others observed exchange reactions between halocarbons and metallic tagged fluorides. Thus, reaction scheme (2) could be written explicitly in chemical terms in this way

$$CHCl_2F + AlF_3 \rightarrow CHClF_2 + AlClF_2$$
$$CHCl_2F + AlClF_2 \rightarrow CHCl_3 + AlF_3$$
$$CHClF_2 + AlF_3 \rightarrow CHF_3 + AlClF_2$$
$$CHClF_2 + AlClF_2 \rightarrow CHCl_2F + AlF_3$$

Intermediate activated states of these halogen exchange reactions could be formed by coordination on aluminum of a halogen atom from the reacting molecule



$$\overset{F}{\underset{F}{-\overset{|}{\underset{|}{Al}}}} + CHCl_2F \rightarrow \left[\overset{F}{\underset{F}{-\overset{|\,\ominus}{\underset{|}{Al}}-Cl}} \quad \overset{\oplus}{CHClF}\right] \rightarrow \overset{Cl}{\underset{F}{-\overset{|}{\underset{|}{Al}}}} + CHClF_2$$

The modified active center of the catalyst is transformed back to the original one by another exchange reaction, opposite to the first one. This mechanistic picture seems not only more consistent with pseudo-first-order kinetics but even much more simple than that implying chemisorption of reacting molecules, halogen exchange reaction between adsorbed species, and desorption of products. This last picture must account for all the possible exchange reactions between adsorbed species: for instance, even for the reaction

$$(CHCl_2F)_{ads} + (CHClF_2)_{ads} \rightarrow CHCl_3 + CHF_3$$

In our mechanistic picture, halogen exchange reactions between the same or different chemisorbed species result from balanced halogen exchange reactions between a reacting molecule and catalyst. In this context, the catalyst can be regarded as a constant level reservoir of halogen atoms with high exchanging potential.

Our catalyst has been proved to be effective not only in disproportionation but also in fluorination reactions of hydrocarbons and chlorocarbons. The outlined mechanistic hypothesis seems to be a promising starting point for kinetic investigation on this broader class of reactions and structural analysis methods may provide suitable means for the treatment of these complex kinetic systems.

ACKNOWLEDGMENT

Fruitful remarks and suggestions by Dr. J. Wei are gratefully acknowledged.

REFERENCES

1. Wei, J., and Prater, C. D., *Advan. Catalysis* **13,** 203 (1962).
2. Haag, W. O., and Pines, H., *J. Am. Chem. Soc.* **82,** 387, 2488 (1960).
3. Silvestri, A. J., and Prater, C. D., *J. Phys. Chem.* **68,** 3268 (1964).
4. Miller, W. T., *J. Am. Chem. Soc.* **72,** 705 (1950).
5. Boggs, J. E., and Brockway, L. D., *J. Am. Chem. Soc.* **77,** 3444 (1955).
6. Gens, T. A., and Wethington, J. A., *J. Am. Chem. Soc.* **79,** 1001 (1957).