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The Catalytic Exchange of Iodine in Alkyl Iodides

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The exchange of iodine between ethyl and propyl iodides has been studied over Cu, Fe, Ni, Pd, Rh, and Ir powder catalysts in a flow reactor at temperatures less than 200°C. The exchange between ethyl iodide and methyl, butyl, and isopropyl iodides was studied over Rh. Decomposition, accompanied by catalyst poisoning, occurred over metals having high heats of formation of the corresponding metal iodide such as Ni and Fe. The energy of activation for the exchange between ethyl and propyl iodides over various metals was in the range 11.6–12.7 kcal/mole. For ethyl iodide with other alkyl iodides over Rh the energy of activation increased slightly with the chain length from 11.2 to 14.4 kcal/mole. The rates suggest a Langmuir-Hinshelwood mechanism, but the heats of adsorption apparently decrease with increasing surface coverage. There is good correlation between relative exchange activity and both relative hydrogenation efficiency and *d* character of the catalysts.

INTRODUCTION

Heterogeneous catalytic exchange reactions involving halogens have not been studied extensively. With metal catalysts the problem is complicated by formation of surface metal halides (*1*, *2*).

One may minimize surface metal halide formation by, first, exchanging the halogen between two alkyl halides instead of between the alkyl halide and its elemental or hydrogen halide form, thus decreasing the ability of the halogen to attack the surface; and, second, by exchanging iodides instead of chlorides or bromides, since the formation of the metal iodide is less favored thermodynamically; and, finally, by using noble metals as catalysts where the heat of formation of the metal iodide is approximately 15 kcal/mole or less in comparison to the value of 45 kcal/mole characteristic of metals such as Fe and Ni.

EXPERIMENTAL

Materials

Chemicals. The reactants were obtained from the Baker Corporation, purified in a Todd Distillation Column, and checked for purity by refractive index.

The isotope used was ^{125}I obtained carrier-free as NaI in basic sulfite solution from Nuclear Science and Engineering Corporation. This was exchanged with ethyl iodide in alcohol solution to form radioactive ethyl iodide. This was the only isotopic carrier used.

Catalysts. The catalysts were obtained from United Mineral and Chemical Company. The Cu and Ir were in powder form while the Fe, Ni, Pd, Pt, were sponges. However, the sponges were indistinguishable from the powders in gross physical form. Except for Ir, which was 99.8% pure, the rest of the catalysts were reported to be at least 99.999% pure.

These catalysts were used as obtained except for a 4-day reduction with H_2 at flows of approximately 60 cc/min. The temperatures used for reduction were Cu, 325°; Ir, 300°; Fe, 425°; Ni, 325°; Pd, 150°; Pt, 125°C. Following reduction the metals were left at the reduction temperature overnight in a N_2 stream to remove H_2 from the surface. Three to 5 g of catalyst was used. This amount of catalyst gave approximately a

1 to 1.5 cm depth of catalyst bed in a reactor of 12-mm ID.

Equipment

Reaction apparatus. A simple Pyrex flow reactor was used in this study. Purified N_2 was used as the carrier gas. Reactants were admitted to a vaporization chamber with a constant-rate syringe drive from which they were carried to a preheated region before passage over the catalyst bed. After reaction the reactants and products were condensed from the stream with a Dry Ice–acetone bath.

Gas chromatograph. Separation of ethyl iodide from the other alkyl iodide was accomplished with a simple gas chromatograph. This consisted of a 7-mm ID by 250 cm long glass column wrapped with resistance wire for heating. The packing was di-2-ethylhexyl sebacate (std. conc.) obtained from the Burrell Corporation. Detection was with a thermal conductivity cell connected to a Leeds & Northrup recorder.

Radioactivity counter. A Radiation Instrument Development Laboratory Scintillation Counter was used, consisting of a Model 200-S counter, Model 115 pulse-height analyzer, and NaI(Tl) well-type crystal detector. Counts were always in excess of 10^6 so that the standard deviation in the count rate is reduced to less than 0.1% (*3*).

Procedure

Diffusion was eliminated as the rate-controlling step by the usual method of varying the linear flow rate and catalyst volume proportionally.

Thermal exchange was checked by passing the reactants through the reactor packed with glass wool and found to be insignificant at temperatures less than 200°C.

To account for the small amount of exchange (less than 1%) which occurs on the gas chromatographic column, a mixture equivalent to the reaction mixture was injected by syringe into the gas chromatograph. After separation the ethyl iodide was selectively condensed from the stream, placed in a constant-temperature bath, and pipetted into a counting tube. The count rate per volume of this ethyl iodide was used as the standard.

Finally, in the runs for reaction rate measurements, the reaction was started in the reaction apparatus and after steady state was achieved, collection of reactants and products continued until approximately 0.4 ml was collected. This was injected into the gas chromatograph and the procedure followed as for the standard. The decrease in the count rate per unit volume was used to obtain the reaction rate.

During the determination of the energy of activation the temperature was raised alternately above and below the mean temperature to detect changes in catalytic activity.

KINETICS

In view of the chemical similarity of the reactants, it is natural to assume that if one reactant is adsorbed the other must be also, though not necessarily to the same extent. The assumption leads to competitive adsorption and a Langmuir-Hinshelwood mechanism.

The reaction is

$$\begin{array}{lllll}
\mathrm{EI}^* & +\,\mathrm{AI} & \underset{k'}{\overset{k}{\rightleftharpoons}}\,\mathrm{EI} & +\,\mathrm{AI}^* & \\
fp_e & p_a & (1-f)p_e & 0 & t=0 \\
fp_e - p_x & p_a - p_x & (1-f)p_e + p_x & p_x & t=t
\end{array}$$

Since the total number of moles remains constant, it is convenient to express the quantities of reactants in terms of their partial pressures, as shown above, where p_e is the partial pressure of both species of ethyl iodide ($\mathrm{EI} + \mathrm{EI}^*$) and p_a, that of the other alkyl iodide ($\mathrm{AI} + \mathrm{AI}^*$); f, is the fraction of labeled ethyl iodide (EI^*) in the original reactant ethyl iodide; and p_x, the partial pressure of EI^* reacted in time t.

If the Langmuir-Hinshelwood (L-H) mechanism is valid, then the net forward rate of reaction of the labeled species *only* is

$$r^* = \frac{dp_x}{dt} = k\theta_e^*\theta_a^{-*} - k'\theta_e^{-*}\theta_a^* \qquad (1)$$

where θ_e^* is the fraction of the catalyst surface occupied by labeled ethyl iodide; θ_a^{-*}, that covered by unlabeled alkyl iodide; θ_e^{-*}, that covered by unlabeled ethyl iodide; and θ_a^*, that covered by labeled alkyl iodide.

If θ_e and θ_a are the fractions of catalyst surface occupied, respectively, by *both* species of ethyl and alkyl iodide, then at time t

$$\theta_e^* = \frac{fp_e - p_x}{p_e}\theta_e, \quad \theta_e^{-*} = \frac{(1-f)p_e + p_x}{p_e}\theta_e$$

$$\theta_a^* = \frac{p_x}{p_a}\theta_a, \qquad \theta_a^{-*} = \frac{p_a - p_x}{p_a}\theta_a$$

Assuming no isotope effect, $k = k'$ and the rate becomes

$$r^* = k\theta_e\theta_a \times \left[\frac{fp_e - p_x}{p_e}\frac{p_a - p_x}{p_a} - \frac{(1-f)p_e + p_x}{p_e}\frac{p_x}{p_a}\right] \qquad (2)$$

With low concentrations of label $f \ll 1$ and $p_x \ll p_a$, p_e; so that the equation can be simplified to

$$r^* = k\theta_e\theta_a\left[\frac{fp_e - p_x}{p_e} - \frac{p_x}{p_a}\right] \qquad (3)$$

If the activity of ethyl iodide at $t = t$ is defined as

$$\alpha = \frac{fp_e - p_x}{p_e}$$

which becomes at $t = 0$

$$\alpha_0 = f$$

then

$$p_x = (\alpha_0 - \alpha)p_e \qquad (4)$$

Substituting p_x from (4) into (3) gives

$$r^* = k\theta_e\theta_a(1/p_a)[\alpha(p_a + p_e) - \alpha_0 p_e] \qquad (5)$$

and since

$$r^* = dp_x/dt = -p_e(d\alpha/dt)$$

$$d\alpha/dt = -k\theta_a\theta_e(1/p_ap_e)[\alpha(p_a + p_e) - \alpha_0 p_e] \qquad (6)$$

In our experiments, count rates of ethyl iodide as a function of t were measured (or converted to) count rates for a fixed amount of ethyl iodide so that the observed count rates are related to the activity by a simple constant of proportionality whose value depends upon the counting efficiency. Thus

$$C_0 = q\alpha_0, \qquad C = q\alpha$$

where C_0 and C are the count rates at $t = 0$ and $t = t$. Substituting for α_0 and α gives

$$dC/dt = -k\theta_a\theta_e(1/p_ap_e)[C(p_a + p_e) - C_0p_e] \qquad (7)$$

In a steady state flow reactor, as in these experiments, and at constant temperature p_a and p_e—and therefore θ_a and θ_e—do not change as the reaction mixture passes through the catalyst bed, and are therefore not functions of time. For the same reason p_a and p_e are the inlet partial pressures. Integration of (7) then gives

$$\ln\left[\frac{C_0p_a}{C(p_a + p_e) - C_0p_e}\right] = k\theta_a\theta_e\frac{p_a + p_e}{p_ap_e}t \qquad (8)$$

Equation (8) has been tested experimentally by plotting the left member as a function of $[(p_a + p_e)/p_ap_e]t$ for constant temperatures and for various values of p_a and p_e. A few representative plots are shown in Fig. 1. It will be observed that the plots are straight lines passing through the origin as required by Eq. (8).

Values of the adsorption coefficients can be obtained from the values of $k\theta_e\theta_e$ at constant temperature.[*] If a L-H mechanism is operative and the Langmuir isotherm applies

$$k\theta_e\theta_a = k\frac{B_eB_ep_ap_e}{(1 + B_ep_e + B_ap_a)^2} \qquad (9)$$

and any set of three corresponding values of p_ep_a and $k\theta_e\theta_a$ can be solved simultaneously

[*] In the course of this study, kinetic data were obtained partly by the use of the "full course" rate equation (8) and partly from initial rate data by the usual procedure of extrapolating rates to zero reaction time, which of course amounts to neglecting the reverse reaction. No clearly significant differences between results obtained by these two methods were observed and the method used is not distinguished in the reported results. However, where any differences were found, the results obtained from the "full course" data were preferred since the initial rate data suffers from the usual difficulty of construction of tangents and heavily weights data obtained at low conversions where the experimental error is largest.

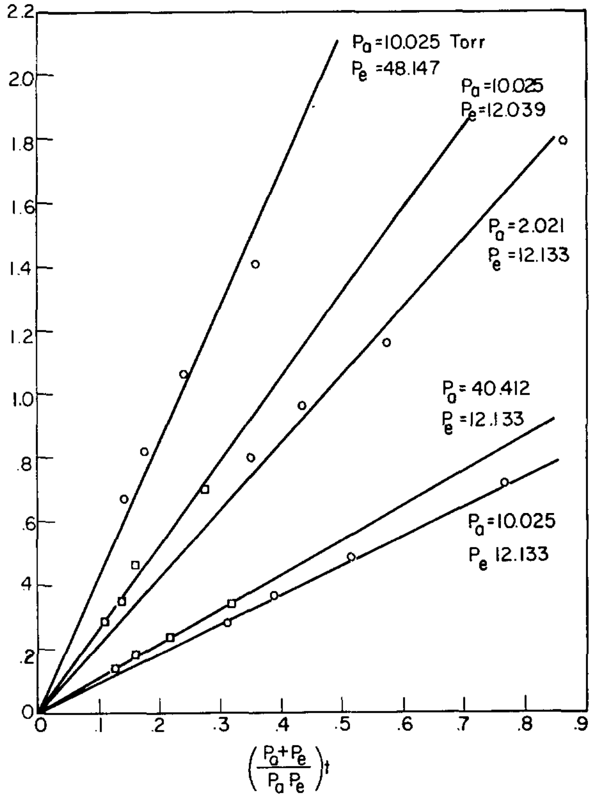

FIG. 1. Test of the rate equation: EI + PrI over Rh at 80°.

for k, θ_e, and θ_a. It was noted, however, that the values of the adsorption coefficients obtained from Eq. (9) by this procedure depend upon the pressures used for their calculation. This result is not surprising since it is well known that heats of adsorption—and hence adsorption coefficients—vary with surface coverage and that the Langmuir equation generally does not fit adsorption data over wide ranges of coverage. Under the circumstances, the reported values of θ and B can only be regarded as averages corresponding to the temperature and pressure ranges used for their calculation.

The energy of activation can be obtained from the variation of $k\theta_a\theta_e$ with temperature provided the relationship between the θ's and T is known. Unfortunately the variation of the adsorption coefficients with pressure precludes a quantitative demonstration of the validity of the L-H mechanism.

There is other evidence that a competitive surface mechanism is operative. The salient feature of a L-H mechanism is the prediction of a maximum in rate as the partial pressure of one of the reactants is varied. Figure 2 shows an example of the variation of the rate of exchange between ethyl iodide and propyl iodide as a function of the pressure of the propyl iodide. The maximum in the case of propyl iodide is clearly shown in Fig. 2 and obviously maxima must also exist in the cases of butyl and isopropyl iodides, since the rates necessarily pass through the origin and the reaction orders are negative over the measurable pressure range, although the positions of these maxima are at pressures too low for accurate rate measurements. Table 1 compares the observed maxima for all the systems with those calculated from the well-known relationships for the rate maxima:

$$p_a = \frac{1 + B_e p_e}{B_a}, \qquad p_e = \frac{1 + B_a p_a}{B_e}$$

The agreement between the positions of calculated and observed maxima is as good as could be expected in view of the uncertainty in the adsorption coefficients, and is persuasive evidence that a competitive mech-

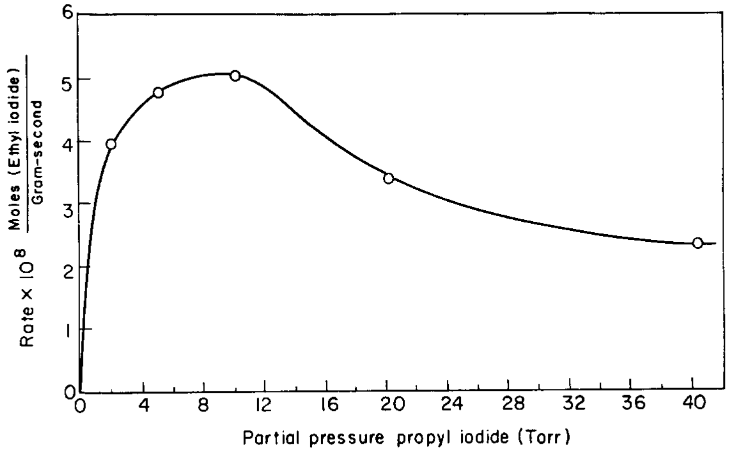

FIG. 2. Variation of initial rate as a function of pressure: EI + PrI over Rh at 80°.

anism is operative, although the Langmuir expression for θ_a and θ_e, since it assumes adsorption coefficients independent of coverage, is only approximately valid.

Further indications of the competitive character of the mechanism appear from inspection of Table 2. Note that the adsorption coefficient of EtI diminishes as it is forced to compete with larger molecules, which are apparently able to preempt sites with higher heats of adsorption.

Although the use of the Langmuir expression makes the result approximate, the behavior of the L-H mechanism as a function of temperature is worth examining. If k, θ_a, and θ_e of Eq. (8) are each separated into pre-exponential and exponential factors, we have

$$k\theta_a\theta_e = A_h \exp\left(\frac{-E_h}{RT}\right) \frac{A_a \exp(\lambda_a/RT)p_a A_e \exp(\lambda_e/RT)p_e}{[1 + A_a \exp(\lambda_a/RT)p_a + A_b \exp(\lambda_e/RT)p_e]^2} \qquad (10)$$

where E_h is the true heterogeneous energy of activation and A_h, A_a, and A_e are the preexponential factors, or

$$\ln k\theta_a\theta_e = \ln A_h A_a A_e p_a p_e + \frac{\lambda_a + \lambda_e - E_h}{RT} - 2 \ln (1 + A_a \exp(\lambda_a/RT)p_a + A_e \exp(\lambda_e/RT)p_e)$$

In experiments in which p_a and p_e are constant, the first term of the right member vanishes upon differentiation* and

$$\frac{d \ln k\theta_a\theta_e}{d(1/T)} = \frac{\lambda_a + \lambda_e - E_h}{R} - 2\,\frac{A_a \exp(\lambda_a/RT)(\lambda_a/R)p_a + A_e \exp(\lambda_e/RT)(\lambda_e/R)p_e}{1 + A_a \exp(\lambda_a/RT)p_a + A_e \exp(\lambda_e/RT)p_e} \qquad (11)$$

The second term of the right member of (11) is recognizable as

$$-2[\theta_a(\lambda_a/R) + \theta_e(\lambda_e/R)]$$

so that

$$\frac{d \ln k\theta_a\theta_e}{d(1/T)} = \frac{\lambda_a + \lambda_e - E_h}{R} - \frac{2}{R}(\theta_a\lambda_a + \theta_e\lambda_e) \qquad (12)$$

We have carried out a series of runs at various temperatures with p_a and p_e constant at 12.63 mm and 15.17 mm, respectively. A typical plot of the results is shown in Fig. 3.

All the results of plotting $\ln k\theta_a\theta_e$ vs. $(1/T)$ are shown in Figs. 4 and 5.

TABLE 1
CALCULATED AND OBSERVED MAXIMUM RATES OVER RHODIUM CATALYST

Reactants	T (°C)	Pressure at maximum rate			
		p_e(mm)		p_a(mm)	
		Calc.	Obs.	Calc.	Obs.
EtI, MeI	80°	11	2	37	>60
EtI, PrI	80°	87	>48	5	10
EtI, BuI	100°	80	>48	3	2
EtI, isoPrI	70°	970	>48	3	2

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* Making the customary assumption that the temperature dependence of the pre-exponential term is negligible in comparison with that of the exponential term.

TABLE 2
EXPERIMENTAL DATA

Catalyst	Reactants	Order at (°C)		B		θ		Pressure range (torr)		E_{calc}(kcal/mole) (°C-°C)
		EI	AI	EI	AI	EI	AI	EI	AI	
Ir	EtI, PrI	0.20	0.39 (130°)	0.11	0.094	0.41	0.29	2–48	10–40	12.3 (100–140°)
Pt	EtI, PrI	0.55	0.11 (190°)	0.035	0.068	0.27	0.43	2–12	10–40	11.2 (160–200°)
Pd	EtI, PrI	0.58	0.22 (140°)	0.042	0.11	0.24	0.53	2–48	2–10	13.0 (100–150°)
Cu	EtI, PrI	0.58	0.49 (170°)	0.011	0.040	0.12	0.29	7–38	6–31	12.2 (140–180°)
Rh	EtI, MeI	−0.05	0.40 (80°)	0.23	0.10	0.54	0.31	12–47	3–61	12.0 (60–100°)
Rh	EtI, PrI	0.62	0.07 (80°)	0.046	0.30	0.13	0.69	12–48	2–10	12.8 (60–100°)
Rh	EtI, isoPrI	0.98	−0.11 (70°)	0.0082	0.69	0.012	0.86	2–48	2–10	11.2 (50–100°)
Rh	EtI, BuI	0.71	−0.25 (100°)	0.072	0.55	0.14	0.74	2–48	2–9	14.4 (70–110°)

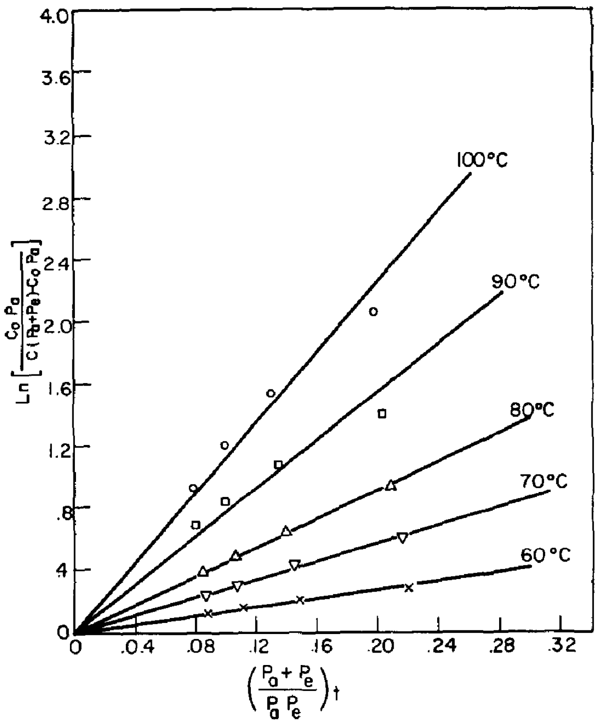

FIG. 3. Effect of temperature on rate: EI + PrI at 60–100°.

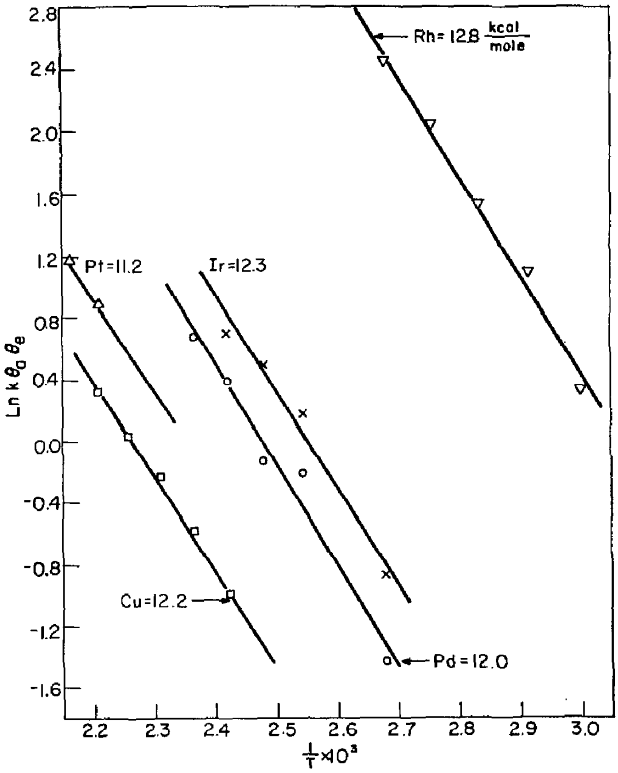

FIG. 4. Arrhenius plots for various catalysts: EI + PrI.

The observation that the slopes of Figs. 4 and 5 are constant are surprising in view of the expected temperature dependence of the term

$$\frac{2}{R}(\theta_a\lambda_a + \theta_e\lambda_e)$$

in Eq. (12). Possible explanations are as follows: (1) The term is not actually constant but is small compared with the first term. Since θ_a and θ_e are apparently not particularly small, λ_a and λ_e must be small compared with E_h. In this case, $E_{calc} \approx E_h$. (2) The term is constant but not necessarily small. This would imply internal compensation: e.g., an increase in heat of adsorption with a decrease in θ. Since this kind of compensation is to be expected it cannot be assumed that heats of adsorption are small, but it is worth noting that in any case—to the degree that the Langmuir expression is a useful approximation—$E_{calc} = E_h - \lambda_a(1 - 2\theta_a) - \lambda_e(1 - 2\theta)$, so that for values of θ_a and θ_e not too far from 0.5, $E_{calc} \approx E_h$.

Results and Discussion

The principal experimental results are summarized in Table 2.

The copper catalyst changed color during the initial runs; check runs, however, showed no change in catalytic activity.

Palladium slowly lost activity during the initial runs, possibly due to incomplete removal of hydrogen dissolved during reduction. Overnight exposure to a slow flow of reactants at 100°C stabilized its catalytic activity.

Platinum was originally rather unreactive. Raising the temperature to 200°C resulted in decomposition of the iodides and catalyst poisoning. Upon repetition of reduction the activity rose to two to three times the original value. In subsequent runs the catalytic activity was initially low, but slowly increased during the run. The energy of activation reported is that corresponding only to the two lowest temperatures, and is probably less reliable than the other values.

Over rhodium, ethyl and isopropyl iodides underwent slight decomposition as evidenced by faint tinges of iodine color in the products. It is not thought that the decomposition was sufficient to substantially affect the results.

The catalysts were tested for residual radioactivity following the runs. None of the noble metals showed activity, indicating no substantial metal iodide formation. Nickel and iron, however, showed appreciable residual activity and their catalytic activities decreased substantially during a series of runs. No quantitative data are reported for these catalysts.

The most striking feature of the results is the constancy of the energy of activation. Since the uncertainty in E_{calc} probably amounts to ±0.5 kcal/mole (±1 kcal/mole in the case of Pt) it is not certain that there are any real differences with the possible exception of butyl iodide over rhodium. It is therefore very likely that the activation energy observed refers in every case to the same process.

If this assumption is justified, and if E_{calc} approximates E_h, then E_{calc} is that corresponding to the breaking of one C–I and one C–I* bond and the formation of two energetically equal bonds. All of the species involved are, of course, adsorbed during this rate-determining step, and $\Delta H = 0$.

The fact that the energy of activation over the same catalyst is practically independent of the reacting species is thus easily understandable since only the strength of the adsorbed C–I bond is significant.

That the energy of activation for the same reacting species over different metals changes so little is somewhat surprising since it might be supposed that adsorption on different metals could markedly affect the strength of the adsorbed C–I bond. Similar observations for the noble metals are not uncommon, however (*4*). That copper is not different is probably to be attributed to the fact that the heat of formation of copper iodide is quite similar to that of the noble metals, so that its effect in weakening the C–I bond may not be much different. This explanation is at least consistent with the observation that metals like iron and nickel, which form very much more stable iodides, behave in a very different way, apparently extracting iodine from the alkyl iodides, exhibiting

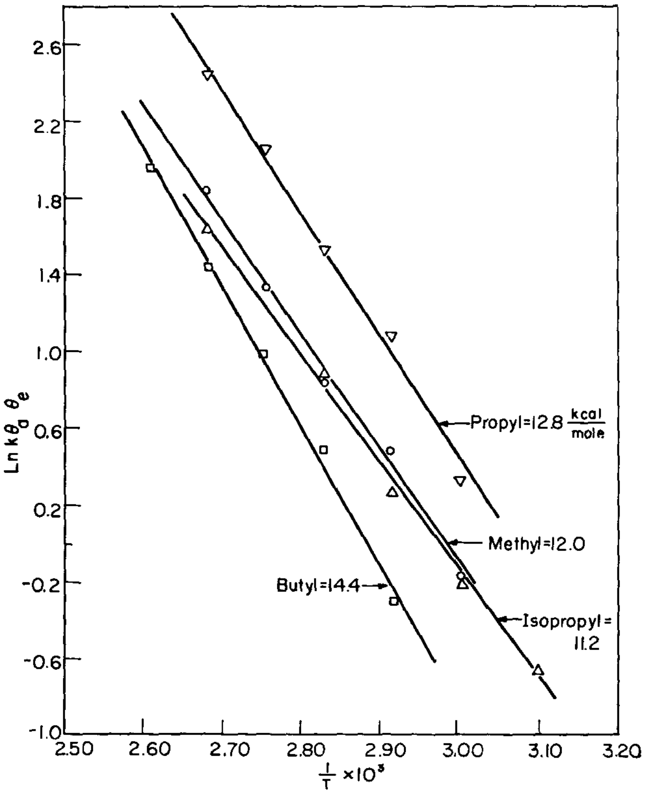

FIG. 5. Arrhenius plots for various reactants over Rh.

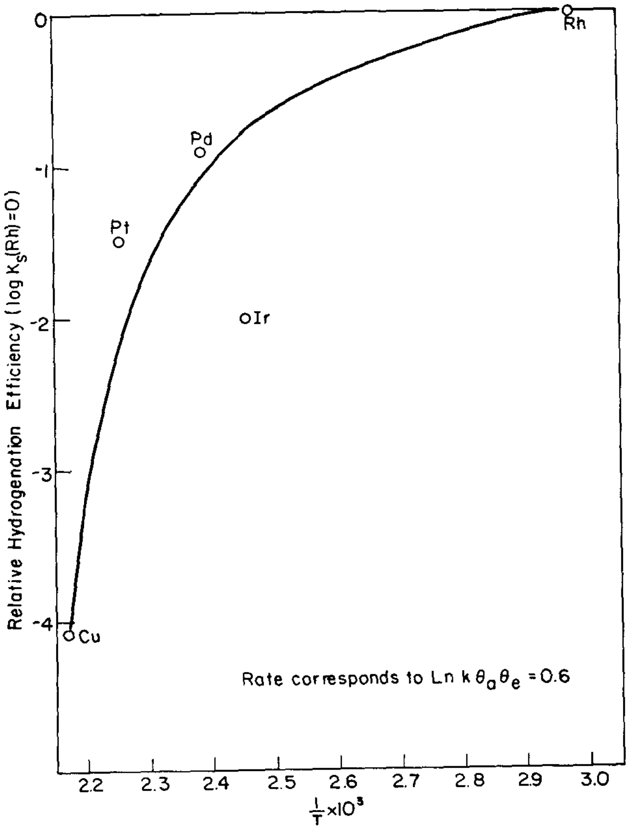

FIG. 6. Correlation of catalytic activity with relative ethylene hydrogenation efficiency.

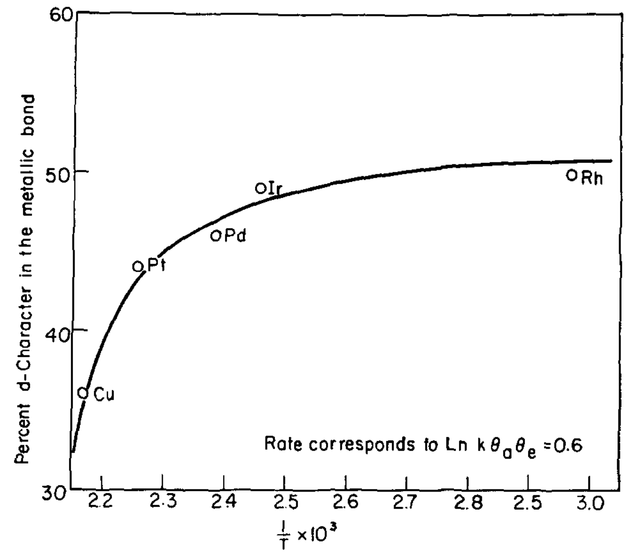

FIG. 7. Correlation of catalytic activity with *d* character.

residual radioactivity, and becoming poisoned for further catalytic activity.

Although the influence of the alkyl radicals on the energy of activation is observed to be small, their adsorption properties have an effect on the scenario of the catalytic process. As is apparent from the trends of adsorption coefficients and from the changes in order of reaction, increasing chain length corresponds to stronger adsorption, which in turn must reflect participation by the alkyl carbon atoms in adsorption. This effect is most pronounced in the case of butyl iodide and may account in an indirect way for the slightly increased energy of activation. Because the alkyl group contributes to the strength of adsorption, it is likely that the choice of sites upon which adsorption occurs is influenced at least in part by the preference of the alkyl group. In cases in which the influence of the alkyl group is strong, this effect may result in the selection of some sites which are not most favorable for weakening the C–I bond.

Attempts to correlate catalytic activities of these metals with other data are modestly successful. Obviously the nearly constant energies of activation cannot be correlated with percent *d* character which runs from 36% in copper to 50% in rhodium (*5*), nor with relative ethylene hydrogenation efficiency (*6*) running from 0 for rhodium to −4.1 for copper.

On the other hand, if relative catalytic activity is expressed as the value of $1/T$ for equal values of $k\theta_a\theta_e$ ($\ln k\theta_a\theta_e = 0.6$ in this instance) the correlation with relative hydrogenation efficiency is quite good (except in the case of iridium) and the correlation with percent *d* character is remarkably good (Figs. 6 and 7).

REFERENCES

1. ADAM, J., COEKELBERGS, R., FRENNET, A., AND GOSSELAIN, P. A., *J. Chem. Phys.* **24**, **1267** (1956).

2. CAMPBELL, J. S., MOSS, R. L., AND KEMBALL, C., *Trans. Faraday Soc.* **56**, **1481** (1960).

3. OVERMAN, R. T., AND CLARK, H. M., "Radioisotope Techniques," p. 116. McGraw-Hill, New York, 1960.

4. BOND, G. C., "Catalysis by Metals," p. **272.** Academic Press, New York, 1962.

5. PAULING, L., *Proc. Roy. Soc.* (*London*) **A196,** 343 (1949).

6. BOND, G. C., "Catalysis by Metals," p. **246.** Academic Press, New York, 1962.