where m, determined from Fig. 1, has a value of approximately 0.048. In Eq. (6) the effects of changing catalysts is accounted for by using a reference rate measurement on the isopropylbenzene dealkylation. Also the influence of different alkyl groups is now completely separated from the catalyst effects and is linearly related to the heats of formation of the rate-determining carbonium ion.

It is noteworthy and perhaps conspicuous that this successful correlation of reactant structure effects does not require modeling adsorption equilibrium in the same way that surface rearrangement was modeled by the carbonium ion formation. In general, however, the application of linear free energy relations to heterogeneous catalysis may require modeling both adsorption equilibrium and surface rearrangement. For the reaction series considered here Mochida and Yoneda have shown empirically and theoretically, in deriving Eq. (2), that alkyl group changes have no influence on the adsorption equilibrium constants. At the same time they have shown how the surface rearrangement can be modeled. Thus in this case, the use of linear free energy relations has led to detailed knowledge of both the adsorption and surface rearrangement processes. Because of the complexity of heterogeneous catalytic reactions, linear free energy relations can be expected to be particularly useful in isolating the adsorption, reactant, and catalyst effects. Their utility lies not so much in making predictive correlations but in dissecting the various steps in the catalytic process and testing proposed models for each step. This general problem will be discussed in a later communication.

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Catalytic Behavior of Organic Semiconductors

1,2-Butene Isomerization of Violanthrene A–Iodine Charge-Transfer Complex

The isomerization of 1-butene to 2-butene has been reported to proceed in the presence of acid-base catalysts. This double-bond shift may be accompanied by the abstraction and the addition of protons from and to butene molecules, and by their migration on the catalyst surface. On the basis of these facts, it can easily be inferred that centers in which electrons are depleted offer sites for isomerization.

From these considerations, it is expected that the charge-transfer complexes in which electrons transfer from hydrocarbon would be active in the isomerization of 1-butene to 2-butene. In the complexes, violanthrene A ($C_{34}H_{18}$) reacts with arbitrary amounts of iodine to form an amorphous charge-transfer complex (denoted as VEA-I_2) of a different electrical conductivity as a function of the iodine content (*1, 2*); electrons in violanthrene transfer to iodine.

In this short note, we will present our preliminary results on the double-bond migration of butene on VEA-I_2; we undertook this study as a part of our studies of the catalytic behavior of organic semiconductors (*3*).

About 600 mg of violanthrene A was suspended in 50 ml of benzene, and then refluxed with 5 g of iodine. The suspension was precipitated, thus forming the complex. Since the solubility of violanthrene A in benzene was very small, the increased weight of the precipitate was assumed to be due to the iodine content of the complex formed, from which the composition was determined.* Two samples, containing 3.18 molecules (Sample I) and 2.10 molecules (Sample II) of iodine per molecule of violanthrene A were prepared.

Butene used in this experiment was of a commercially available grade, containing only a small amount of *n*-butane impurities. The catalytic reaction was performed in a Pyrex glass cylindrical vessel placed in an electric furnace, the temperature of which was measured by an ordinary Chromel-Alumel thermocouple. The products were separated in a dimethyl formamide column, and the relative amounts of butene isomers were determined accurately.

The double bond of a butene molecule migrated in the presence of VEA-I_2, as is shown in Fig. 1. 1-Butene was decreased, whereas *cis*- and *trans*-2-butene were increased, during the course of the reaction at 60°C with an initial 1-butene pressure of 100 mm Hg. The rate was enhanced by an increase in the reaction temperature; 20% of 1-butene transferred to 2-butene over 150 mg of VEA-I_2 at 60°C within 14 days, but 10% of 1-butene transferred to 2-butene at room temperature within the same period. 1-Butene transferred with approximately the same probability to *cis*-2-butene and *trans*-2-butene.

In order to consider the effect of the iodine content in the charge-transfer complex, the isomerization was examined at the temperature of 60°C and at the pressure of 100 mm Hg over Samples I and II, as is shown in Fig. 1. The results imply that iodine in the complex strongly affects the rate of isomerization. On the other hand, no trace of hydrogen deuteride was found at 60°C in a mixture of hydrogen and deuterium over the VEA-I_2 samples used here.

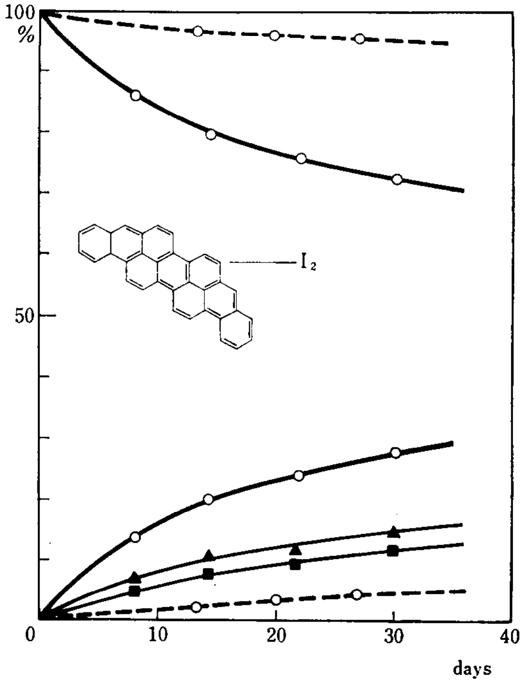

FIG. 1. 1-Butene → 2-butene isomerization of the violanthrene A–I_2 charge-transfer complex: —○—, the isomerization over Sample I (150 mg) at 60°C; —▲—, increase of *trans*-2-butene and —■— increase of *cis*-2-butene over Sample I; ---○--- 1-butene → 2-butene over 150 mg of Sample II at 60°C.

We are planning to determine the dependence of the specific rate of the isomerization on the amount of iodine introduced in the complex in order to obtain further insight into the mechanism of the reaction. It has been reported that the isomerization of the butene molecule occurs on iodine vapor above 200°C, though hardly at all below 100°C in the dark (*4*). In effect, we found that a negligible quantity of 2-butene was evolved by contact with iodine at 60°C, leading us to conclude that the violanthrene-I_2 complex could convert 1-butene to 2-butene.

It is left for future consideration whether iodine is activated by interaction with the

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* The iodine content in the VEA-I_2, as determined by a chemical analysis, agreed with that estimated from the increased weight of the complex.

violanthrene—electron donor— or whether the VEA-I_2 complex is essential for the isomerization.

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Hydrogenation of Conjugated Diolefins with Cobalt(II) Complexes

It has been already shown (*1*) that a number of transition metal compounds, for example, Ti(O-iso-$C_3H_7)_4$, VO(O-*n*-$C_4H_9)_3$, and Cr(acac)$_3$, combined with organometallic derivatives, are soluble catalysts for the hydrogenation of olefins such as cyclohexene, 1-octene, *trans*-stilbene, 2-methyl-2-butene, *trans*-2-pentene, tetramethylethylene, and 1-hexene. Transition metals in Groups IV–VIII, mostly as acetylacetonates or as alkoxides, have been found to be active when combined with, preferably, a trialkylaluminum compound.

In this paper, hydrogenation of butadiene or isoprene by binary catalyst systems of cobalt(II) complexes and aluminum triethyl is reported. Cobalt(II) complexes tried were bis(triphenylphosphine)cobalt(II) dichloride, $[(C_6H_5)_3P]_2CoCl_2$; bis(triphenylphosphine oxide)cobalt dinitrate, $[(C_6H_5)_3PO]_2Co(NO_3)_2$; and tris(pyridine)cobalt dinitrate, $Py_3Co(NO_3)_2$. Cobalt(II) acetylacetonate, Co(acac)$_2$; and bis(salicylaldehyde)cobalt (II), $Co(C_6H_4OCHO)_2$, were also tried.

Cobalt(II) acetylacetonete, Co(acac)$_2$, was prepared (*2*) by heating bis(acetylacetonate)cobalt(II) dihydrate in vacuo for 6 hr at 58°C. The dihydrate was prepared according to the method (*3*) of Charles and Pawlikowski. Bis(salicylaldehyde)cobalt(II), $Co(C_6H_4OCHO)_2$, was prepared (*2*) by heating bis(salcylaldehyde)cobalt dihydrate in vacuo for 12 hr at 58°C. The dihydrate was prepared according to the method (*4*) of Tyson and Adams. Bis(triphenylphosphine) cobalt(II) dichloride, $Co(PPh_3)_2Cl_2$, was prepared (*5*) by reaction of a hot absolute ethanol solution of the anhydrous cobaltous chloride and triphenylphosphine. Bis(triphenylphosphine oxide)cobalt(II) dinitrate $Co(PPh_3O)_2(NO_3)_2$ was prepared (*6*) by the reaction of cobalt(II) nitrate and excess of the triphenylphosphine oxide. Tris(pyridine)cobalt(II) dinitrate, $Co(Py)_3(NO_3)_2$, was prepared (*7*) by the reaction of the methanol solution of cobalt(II) nitrate and pyridine.

The hydrogenation reactions were carried out in an autoclave (100 ml), and all operations were carried out in a nitrogen atmosphere. In general, 2 mmole of cobalt complex, (4 mmole of triphenylphosphine), 10 mmole of aluminum triethyl, 50 ml of benzene as a solvent, and 5.6 g of butadiene (or 6.2 g