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Isomerization of Isobutyraldehyde on Eta-Alumina

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The catalytic isomerization of isobutyraldehyde on eta-alumina has been studied in the temperature range 360–600°C. The main liquid reaction products were methyl ethyl ketone and *n*-butyraldehyde, along with smaller amounts of methyl isopropyl, and diisopropyl ketone. It was shown that the presence of water exerts a pronounced influence on the activity of the catalyst, increasing substantially the amount of methyl ethyl ketone formed. Evidence indicates both major liquid products deriving from isomerizations catalyzed by Brönsted acidity, whereas a combination of basic and Lewis acid sites is believed responsible for the formation of higher molecular weight ketones.

INTRODUCTION

Catalytically induced skeletal isomerizations of substituted aliphatic aldehydes to ketones have been known for some time. Sulfuric acid in various concentrations was employed in the earliest investigations, to effect quantitative isomerization of di- and trisubstituted acetaldehydes to the corresponding isomeric ketones (*1*). In a subsequent paper by Danilov (*2*), quantitative rearrangement of trimethyl (or triphenyl) acetaldehyde to methyl isopropyl ketone (or diphenylmethyl phenyl ketone) was achieved with $Al_2(SO_4)_3$ at 350°C. Ramart-Lucas and Guerlain (*3*) reported on a similar isomerization with infusorial earth at 500–600°C, and Japanese acid earth at 300°C was used by Isimura (*4*) to study the influence of aromatic substitution on the migratory tendency of aryl groups in the isomerization of diaryl acetaldehydes. The literature up to 1956 has been reviewed in an excellent article (*5*).

Isobutyraldehyde, which is produced in considerable quantity as by-product in the oxonation reaction of propylene has a very low commercial value and therefore attracts considerable interest in its economic upgrading. Among the reactions contemplated, isomerization is one of the most promising from an economic standpoint, since the isomeric ketone, methyl ethyl ketone, is a very desirable solvent. A recently issued patent (*6*) describes the vapor phase isomerization of isobutyraldehyde, over silica–alumina or supported phosphoric acid catalyst, in the temperature range 300–600°C using steam as a diluent. The encouraging yield values for methyl ethyl ketone obtained in this work prompted us to report results of a similar investigation carried out with eta-alumina.

EXPERIMENTAL METHODS

Materials

The eta-alumina catalyst (Davidson Chemicals, Toronto) was used in this work after grinding and sieving to 8/25 mesh. Its surface area (BET method, using nitrogen as adsorbate) was found to be 278 m^2/g. The surface acidity of this catalyst was measured using the ammonia-oxidation method developed by Hildebrandt and Skala (*7*). The material showed an acidity of 51 μmoles of NH_3 adsorbed/g of catalyst at a pretreatment and adsorption temperature of 450°C. The corresponding ammonia oxidation maximum was observed at 500°C.

Isobutyraldehyde, as supplied (Anachemia, Montreal, P. Q.; or Eastman Chemicals, Rochester, N. Y.) showed variable quantities (up to 10%) of higher boiling materials, mainly isobutyric acid, and was purified by distillation.

Procedure

Isomerization reactions were studied in a conventional fixed bed flow reactor constructed of 22-mm i.d. Pyrex glass tubing, 40 cm long, and heated electrically, using a proportional controller (Guardsman-West, Gananoque, Ont.). The temperature was measured with a thermocouple inserted in a well positioned in the center of the reactor and extending the length of the catalyst bed. For each experiment, the reactor was charged with 20 g of fresh catalyst supported on a plug of glass wool. The remaining length of the reactor served as a preheating zone, and was filled with glass beads. Pretreatment of the catalyst involved heating under a slow stream of dry nitrogen up to the required reaction temperature within 1 hr. All reactions were carried out with vaporized feedstocks; water was vaporized in an electrically heated tube; whereas isobutyraldehyde was vaporized in the top section of a steam-heated spiral condenser. Higher boiling materials in the feed were allowed to accumulate at the bottom of the condenser and were withdrawn at intervals when necessary. Adjustment of feed composition and rate was accomplished with two micropumps (F. A. Hughes, Epsom, England). The reaction products were collected using a water condenser and directly subjected to glc analysis. Noncondensable gases were intermittently analyzed by glc and measured with a wet test meter.

All experimental data were taken under steady-state conditions. For this purpose, a certain composition was passed over the catalyst at the required temperature for 5 hr. The products were then collected over a period of 10 min.

The conventional definitions for conversion (percentage isobutyraldehyde converted) and selectivity (percentage conversion to respective compound × 100 divided by percentage of total conversion) were employed and are based on weight percent of feed. In this work, contact time (sec) is defined as the volume of catalyst bed (ml) divided by the rate of flow of gaseous feed (ml/sec).

Analysis

Quantitative analysis of the condensable reaction product was carried out on a Carbowax 600 column (20 ft × ¼ in. of 25% Carbowax 600 on chromosorb W, HMDS treated, 60/80 mesh) installed in a Perkin–Elmer Model 154 gas chromatograph equipped with a thermistor type thermal conductivity detector. Column temperature was 110°C, helium flow, 60 ml/min. The following retention times, expressed as a ratio (isobutyraldehyde = 1.0) were found: acrolein, 1.14; methacrolein and *n*-butyraldehyde, 1.28; methyl ethyl ketone, 1.44; methyl isopropyl ketone, 1.62; diethyl ketone, 1.96; diisopropyl ketone, 2.10; isobutyl isobutyrate, 2.90; water, 3.07; isobutanol, 3.20; and *m*- and *p*-xylene, 3.78. To separate methacrolein and *n*-butyraldehyde, the temperature of the column was lowered to 70°C. The identity of all of the above compounds was confirmed by separate collection of each peak and comparison of their respective infrared and mass spectra with those of authentic samples.

Noncondensable gases (hydrogen, carbon monoxide, methane, propane, propylene) were analyzed on silica gel and propylene carbonate–squalane columns.

RESULTS

Reaction Studies

Acid-catalyzed isomerization of isobutyraldehyde, using eta-alumina, gives methyl ethyl ketone and *n*-butyraldehyde as the major liquid products, together with considerable quantities of decomposition and higher molecular weight condensation products.

The presence of water in the feed had a pronounced influence on the amount of methyl ethyl ketone produced as the corresponding data (runs 23 and 89) in Table 1 show. Water constituted the major liquid by-product in the run without water in the feed, and derived most likely from dehy-

TABLE 1
COMPOSITION OF THE ISOMERIZATION PRODUCT OBTAINED WITH ETA-ALUMINA CATALYST

Run:	23	89	80	91	95	101
Reaction temp (°C):	435	440	444	445	572	451
Contact time (sec):	12	12.2	1.1	2.7	1.7	0.67
Molar ratio, water/aldehyde:	0	5.5	5.7	10.0	5.5	6.0
Conversion (wt %):	85	84	19.6	20.7	45.6	16.5
Selectivity (wt %)						
Gaseous products	60	58	58	52	61	50
Water	16.0	—	—	—	—	—
Methyl ethyl ketone	6.6	21.3	28.6	35.3	13.1	30.0
n-Butyraldehyde	0.2	1.2	11.2	8.2	8.4	15.4
Acrolein	—	0.2	—	—	—	—
Methacrolein	—	—	—	—	15.0	—
Diethyl ketone	—	1.4	—	—	—	—
Methyl isopropyl ketone	6.2	4.0	0.2	0.9	0.4	—
Dissopropyl ketone	3.5	5.3	1.9	2.0	0.7	2.9
Isobutyl isobutyrate	—	0.1	—	—	—	0.2
Isobutanol	4.5	3.1	0.5	0.7	1.5	1.9
m- and *p*-Xylene	1.1	3.8	0.5	1.0	—	—
Others	1.8	1.6	—	—	—	—

dration of isobutanol (see below). Correspondingly large quantities of isobutylene were found in the gaseous reaction product; whereas hydrogen, carbon monoxide, and C_3 hydrocarbons (propane and propylene) constituted the major components in the gaseous products of the run containing water in the feedstock.

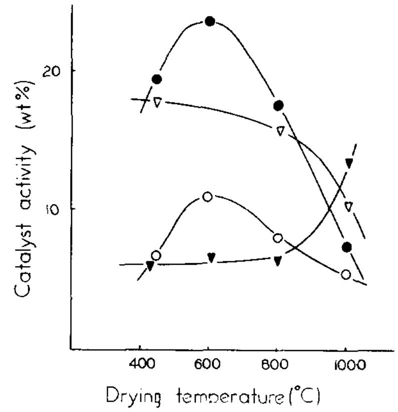

FIG. 1. Influence of drying temperature on catalyst activity: reaction temp, 400–410°C; contact time, 2.0 ± 0.1 sec; molar ratio (water/aldehyde), 5.4 ± 0.1; (○) conversion; (●) selectivity to methyl ethyl ketone; (▽) selectivity to *n*-butyraldehyde; (▼) selectivity to remaining liquid products.

The effect of preheating the catalyst for 2 hr (in dry air) at various temperatures was studied for eta-alumina and the results are shown in Fig. 1. Increasing the drying temperature from 400 to 1000°C clearly reveals a maximum of activity for the skeletal isomerization at approximately 600°C with respect to both conversion and selectivity to methyl ethyl ketone. Catalyst samples preheated at 1000°C showed yield values slightly lower than those at 400°C. Interesting, in this connection, is the high activity of the catalyst (for the decomposition of the aldehyde) after calcination at 1000°C. (Prolonged heating of eta-alumina under these conditions is reported to afford theta-alumina (*8*); however, X-ray diffraction analysis of our calcined catalyst showed the calcination time to be too short to effect this transformation.) Similar drying temperature-activity dependencies have been observed by various workers. For example MacIver *et al.* (*9*) found a maximum activity of eta-alumina, for the skeletal isomerization of pentane-1, at a drying temperature of ca. 650°C; this was similar to the maximum observed by Pines and Haag (*10*) for the isomerization of cyclohexene to methylpentene. Both investigated reactions have been regarded as acid catalyzed.

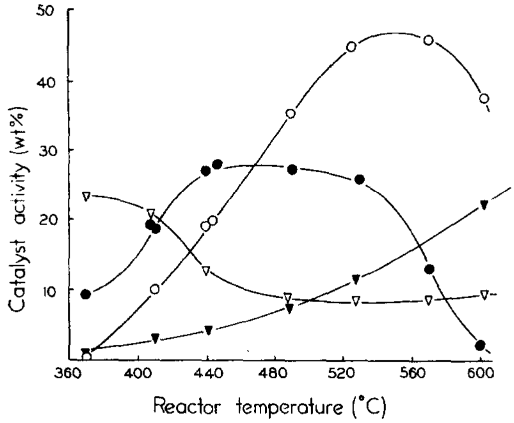

FIG. 2. Influence of reactor temperature on catalyst activity; contact time, 2.3 ± 0.2 sec; molar ratio (water/aldehyde), 5.1 ± 0.1; symbols as in Fig. 1.

The effect of reaction temperature upon the catalyst activity in the skeletal isomerization of isobutyraldehyde was studied as well, and the results, plotted in Fig. 2, show that eta-alumina displays negligible activity below 360°C. The maximum activity with regard to conversion is obtained in the range 540–560°C; whereas the maximum in selectivity towards methyl ethyl ketone occurs around 440–520°C. The initial selectivity towards *n*-butyraldehyde (23% at 360°C) is reduced, with increasing temperature, to a constant value of ca. 8–9%. Above 500°C considerable quantities of methacrolein were observed as well.

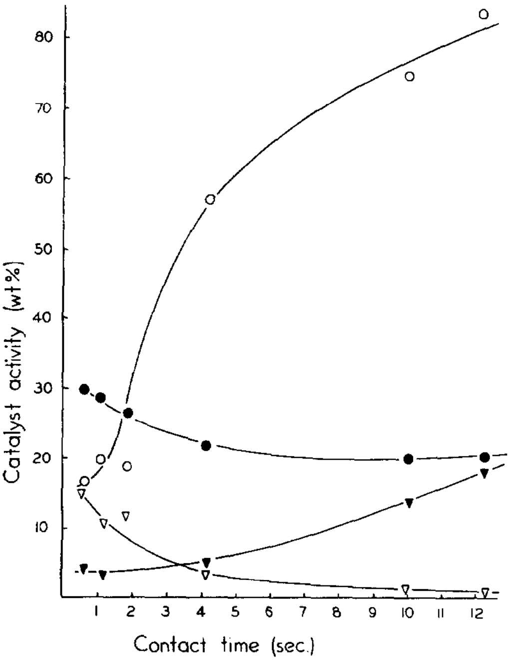

FIG. 3. Influence of contact time on catalyst activity: reaction temp, 440 ± 10°C; molar ratio (water/aldehyde), 5.5 ± 1.0; symbols as in Fig. 1.

Figure 3 shows the effect a change in contact time will have on the catalyst activity. The marked increase in conversion with increasing contact time is associated with only a slight decrease of selectivity towards methyl ethyl ketone.

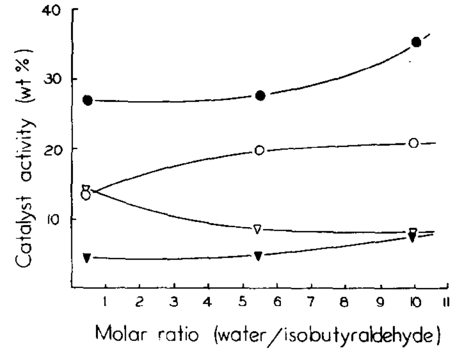

FIG. 4. Influence of feed composition on catalyst activity: reaction temp, 440°C; contact time, 2.7 ± 1.0 sec; symbols as in Fig. 1.

Employing silica–alumina as catalyst, Canter and Perry (*6*) found a molar ratio of water to isobutyraldehyde greater than 5 to be advantageous in obtaining reasonable conversion to methyl ethyl ketone. Although our investigations with eta-alumina showed the necessity of water as an ingredient for the isomerization, a threshold value could not be observed (Fig. 4). The catalyst exhibited only a minor dependence of activity with increasing amounts of water present.

RESULTS

Reaction Products

In addition to methyl ethyl ketone, a variety of products were found in the eta-alumina catalyzed reaction of isobutyraldehyde. Noncondensable gases were analyzed by glc and identified by their respective retention times, whereas most of the liquid compounds were identified by ir and mass spectroscopy after collection via preparative glc. The major components in the reaction gas were hydrogen, carbon monoxide, propane, and propylene, with variable amounts of methane, ethane, and isobutylene present as well. The quantities of the observed liquid reaction products varied considerably with the reaction conditions. The following compounds have been positively identified: acrolein, methacrolein, *n*-butyraldehyde, methyl ethyl ketone, methyl isopropyl ketone, diethyl ketone, diisopropyl ketone, isobutyl isobutyrate, isobutanol, *m*- and *p*-xylene. The distribution of these products in a few selected runs is listed in Table 1.

Discussion

Isobutyraldehyde is, thermally, a very stable compound. Exposure to temperatures, ranging from 400 to 600°C, for the range of contact times used in our investigations, showed only a slight tendency to decomposition, and the complete absence of a thermally induced rearrangement to methyl ethyl ketone. In contact with acidic substances such as silica–alumina (*6*), $Al_2(SO_4)_3$ (*11*) or eta-alumina, the aldehyde undergoes isomerization as well as decomposition reactions, the latter in most cases predominating.

One of the driving forces for this isomerization is apparently the greater thermodynamic stability of the ketone as compared with that of isobutyraldehyde. The corresponding free energy values for the aldehyde are not available; however, by referring to the values for *n*-butyraldehyde (*12*), and taking into account the usual effects of branching, a difference in standard free energy of formation in the order of -8 to -10 kcal can be assumed over the temperature range 300–600°C. Another noteworthy point, in this respect, is the remarkable stability of methyl ethyl ketone, under the isomerization conditions as comparative tests have shown using the ketone as starting material. This then indicates the unlikelihood of a further acid-catalyzed rearrangement.

Formation of *n*-butyraldehyde from isobutyraldehyde requires transfer of a methyl group from its original terminal position (*asym*-CH_2–) to a position in the chain (as CH_2). The evidence shows that it is formed from isobutyraldehyde and not from methyl ethyl ketone or indeed from propylene and CO, as independent experiments have demonstrated. Moreover, the intervention of the catalytic surface is required, since in the absence of a catalyst no reaction is observed. The selectivity curves for methyl ethyl ketone and *n*-butyraldehyde as a function of temperature (Fig. 2) are consistent with the hypothesis that these are alternative pathways, since they exhibit an inverse relationship up to high temperatures where decomposition intervenes.

The formation of methyl ethyl ketone from isobutyraldehyde also involves methyl migration, this time to an adjacent carbon, as CH_3. It also requires the presence of the catalytic surface. If the two products are formed from two different intermediate complexes, implying two types of sites, then their relative abundance or efficacity changes with temperature in a manner indicated by Fig. 2. That they should change in a closely related manner (inverse) must then be regarded as coincidence. Postulation of a common intermediate (*13*) upon the catalytic surface, on the other hand, provides an explanation for the interdependence of the two selectivities. If a single site is involved, then the effect of drying pretreatment should be similar for the two products. This is true in a general way (Fig. 1), although the selectivity to *n*-butyraldehyde shows no distinct maximum. The greater decrease in selectivity for *n*-butyraldehyde as compared to methyl ethyl ketone observed on prolonged contact times (Fig. 3) is not inconsistent with the idea of a common intermediate for both major liquid reaction products but merely reflects the lower stability of the *n*-butyraldehyde under the experimental conditions. On the other hand, the hypothesis of the common intermediate does not appear to offer any obvious explanation for the effect of increased partial pressure of water (Fig. 4).

In addition to the products from the acid-catalyzed rearrangement, numerous compounds were observed in the liquid reaction product and deserve some comment. Isobutanol was detected in small quantities in most of the isomerizations carried out and derived from a simple hydrogenation reaction. It is therefore associated with any reaction liberating hydrogen, such as the decomposition of isobutyraldehyde. Isobutanol, if present, was always accompanied by isobutylene and a mixture of *m*- and *p*-xylene. A 40% yield of isobutylene has recently been reported by Piehl (*14*) for isobutyraldehyde employing MnO_2 at 550°C; no account of the remaining products was given, but it seems likely that part of the hydrogen deriving from decomposition is responsible for the hydrogenation to the alcohol which then undergoes subsequent dehydration to the olefin. A dimerization reaction of isobutylene may account for any *m*- or *p*-xylene observed in our reaction product. The occurrence of various ketones with a carbon number in excess of four most likely (as will be shown later) derives from condensation reactions on a combination of acidic and basic sites.

Although it is convenient to visualize the acid-catalyzed isomerization of isobutyraldehyde to be initiated by Brönsted acidity, the possibility of Lewis acidity being responsible cannot be discounted. The nature of the acidity on eta-alumina still remains in doubt, despite various studies by Pines and Haag (*10*), MacIver *et al.* (*9*), Hirschler (*16*) and others. Generally, it is observed that heating of eta-alumina at 900°C causes a marked decrease in catalytic activity as compared with heating at 500°C, while the reverse is true for acid strength as measured by ammonia chemisorption. This increase in acid strength seems also to be correlated with the considerable amount of water evolved on heating. If now an acid site were indeed required to initiate the reaction, then these observations could be explained on the basis that, when heated at elevated temperature, an eta-alumina surface consists primarily of Lewis-type acid sites rather than Brönsted acid sites. On the basis of results obtained by olefin isomerization reactions, it was concluded by the above workers that no simple relationship exists between catalyst activity and acid strength distribution as given by ammonia chemisorption.

The catalyst activity, as observed in our study as a function of dehydration, corresponds well with that reported by the above workers. The values of conversion and selectivity towards methyl ethyl ketone which were observed using a catalyst preheated at 600°C declined considerably at higher preheating temperatures. The formation of *n*-butyraldehyde, although not displaying a maximum, declined in a similar manner; whereas the selectivity toward liquid products (other than methyl ethyl ketone and *n*-butyraldehyde) increased substantially. Assuming the necessity of Brönsted acid sites for the formation of the two major liquid products, this behavior is readily explained by the fact that, with increasing temperature, part of the existing Brönsted acidity is converted to Lewis acidity which in turn is responsible at least in part for the increased amount of byproducts. In this respect, it may be interesting to note that $AlCl_3$, $BeCl_2$, and $ZnCl_2$, which are considered Lewis acids, when employed for the isomerization of isobutyraldehyde (*11*), afford higher molecular weight products (probably $>C_{10}$ ketones) which differ markedly from those obtained over eta-alumina. Also, condensation reactions of isobutyraldehyde on Li_2O or rare-earth oxides supported on activated alumina have recently been reported (*15*) to produce high yields of diisopropyl ketone together with variable quantities of isobutyric acid. No explanation of the formation of the ketone was offered by the authors. Nevertheless, our results support the postulation of a Brönsted acid-catalyzed formation of methyl

ethyl ketone and *n*-butyraldehyde; whereas existing basic sites probably in combination with Lewis acid sites favor the production of C_5–C_7 ketones.

Although the drying temperature–activity behavior observed for the isomerization of isobutyraldehyde corresponds well with those previously reported, a major difference exists, namely the presence of excess water in our reaction. The pronounced influence, which the presence of water exerted on the composition of the reaction product has already been emphasized. The results would indicate a partial conversion of Lewis acid sites to Brönsted acid sites in the presence of excess water, a behavior which generally has been questioned for aluminas. An additional increase in the amount of water, however, had hardly any further promoting influence on the catalyst activity. On the other hand, it is noteworthy that eta-alumina, on prolonged exposure to a water–aldehyde mixture, effects a marked improvement in the yield, and thus strengthens the assumption of a gradual conversion of acid sites. Thus, it was observed that the selectivities towards methyl ethyl ketone and *n*-butyraldehyde double; whereas the conversion falls to 50%, when reaction times of 2 days (as compared with the standard time of 5 hr) were studied. Longer reaction times (up to 6 days) exhibited no further improvement in the yield pattern, indicating the attainment of a steady-state condition on the catalyst surface. This presumed conversion of acid sites could also be affected by treating the catalyst with steam (for several hours) prior to admission of the water–aldehyde mixture. The yield values obtained with such a catalyst were identical to those obtained with an aged catalyst. Partial coking of the catalyst (~5%) occurs during the initial stages of operation, and probably is associated with Lewis acidity as suggested by Rooney and Pink (*17*). Additional coking, thus reducing further the number of active acid sites, may well be responsible for the decline in conversion with prolonged reaction times.

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REFERENCES

1. DANILOV, S. N., *J. Russ. Phys.-Chem. Soc.* **58,** 129 (1926); *Chem. Abstr.* **21,** 571 (1927); DANILOV, S. N., *Zh. Obshch. Khim.* **18,** 2000 (1948); *Chem. Abstr.* **43,** 4632f (1949).
2. DANILOV, S. N., *J. Russ. Phys.-Chem. Soc.* **61,** 723 (1929); *Chem. Abstr.* **23,** 4670 (1929).
3. RAMART-LUCAS, MME., AND GUERLAIN, J. P., *Bull. Soc. Chim. Fr.* **49,** 1860 (1931).
4. ISIMURA, K., *Bull. Chem. Soc. Jap.* **16,** 196, 252 (1941).
5. DANILOV, S. N., *Reakts. Metody Issled. Org. Soedin.* **4,** 159 (1956); *Chem. Abstr.* **51,** 12026c (1957).
6. CANTER, F. C., AND PERRY, M. A., *U. S. Pat.* 3,384,668 (Eastman Kodak Co.) (1968).
7. HILDEBRANDT, R. A., AND SKALA, H., *J. Catal.* **12,** 61 (1968).
8. STUMPF, H. C., RUSSEL, A. S., NEWSOME, J. W., AND TUCKER, C. M., *Ind. Eng. Chem.* **42,** 1398 (1950).
9. MACIVER, D. S., WILMOT, W. H., AND BRIDGES, J. M., *J. Catal.* **3,** 502 (1964).
10. PINES, H., AND HAAG, W. O., *J. Amer. Chem. Soc.* **82,** 2471 (1960).
11. PLODER, W. H., unpublished results.
12. CHERMIN, H. A. G., *Petrol. Refiner* **40,** 181 (1961).
13. STEVENSON, D. P., WAGNER, C. D., BEECK, O., AND OTVOS, J. W., *J. Amer. Chem. Soc.* **74,** 3269 (1952).
14. PIEHL, D. H., *Chem. Commun.* **1969,** 461.
15. *Can. Pat.* 839,764 (1970), and *U. S. Pat.* 3,410,909 (1968) both Eastman Kodak Co.
16. HIRSCHLER, A. E., *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.* **1969,** B68.
17. ROONEY, J. J., AND PINK, R. C., *Trans. Faraday Soc.* **58,** 1632 (1962).