column,[16] 5 mm. × 30 in., equipped with an electrically heated jacket over a vacuum jacket. The physical properties and ultraviolet absorption maxima (using a Cary Model 11 PMS Spectrophotometer) are given in Table I and the principal infrared absorption bands (using a Beckman IR-2 Spectrophotometer) of the pure liquid in Table III.

*trans*-**Propenylbenzene.**—This material was obtained as a constant boiling, constant refractive index series of cuts from the distillation of the products from the reaction of sodium allylbenzene in pentane with methanol. The distillation was carried out at 20 mm. pressure in an analytical manner using the twisted wire gauze column described above. The physical properties and ultraviolet absorption maxima are given in Table I and the infrared absorption bands in Table III.

The 2,4-dinitrobenzenesulfenyl chloride derivative, m.p. 91.5-92°, was prepared[17] from another sample of *trans*-propenylbenzene, $n^{25}\text{D}$ 1.5468.

*Anal.* Calcd. for $C_{15}H_{13}SN_2ClO_4$: C, 51.06; H, 3.71. Found: C, 51.36; H, 3.87.

**Azeotropes with *n*-Decane.**—Synthetic mixtures of pure *n*-decane, $n^{25}\text{D}$ 1.4098, with *cis*-propenylbenzene and pure *n*-decane with *trans*-propenylbenzene were carefully distilled at 20 mm. pressure in the twisted wire-gauze column. Table IV contains the physical properties and compositions of the azeotropes. The compositions were determined by means of the non-linear, refractive index-composition curves which were based upon the indices of a number of synthetic mixtures.

**Acknowledgment.**—The authors gratefully acknowledge the asistance of Dr. Clair Birdsall of the Linde Air Products Company and Professor Walter F. Edgell of Purdue University in the interpretation of the infrared spectra.

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# Dynamic Structure of Oxide Cracking Catalyst

BY A. G. OBLAD, S. G. HINDIN AND G. A. MILLS

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Recently, Milliken, Mills and Oblad[1] advanced the hypothesis that the catalytic activity of a silica–aluminum cracking catalyst depends for driving force upon the ability of the aluminum ion to undergo a reversible change in coördination number from six to four. This reversible shift in coördination of the aluminum would involve a movement of the oxygen ions of a few tenths of an ångström unit. The purpose of this note is to present experimental evidence that, at cracking conditions, the silica–alumina structure is extremely mobile in the presence of water and such a proposed coördination shift is easily possible.

The exchange of oxygen between water enriched in $O^{18}$ and a silica–alumina cracking catalyst was measured under conditions which the catalyst experiences when used in cracking petroleum. Previous work on such water–oxide exchange[2,3] has been carried out primarily at relatively low temperatures, 100°, and for long times, up to one month. In commercial cracking, temperatures are of the order of 450°. Working at these latter temperatures using a flow system, it was found that remarkably fast exchange occurs so that between 50 and 100% of *all* oxygen of the silica–alumina structure will undergo exchange within a 20-minute period.

## Experimental

A flow system was used, employing conventional apparatus as for catalyst testing.[4] The silica–alumina catalyst was commercial pelleted Houdry Type S-45 previously described.[2] The procedure consisted of passing water enriched in $O^{18}$, at atmospheric pressure, at constant rate through the catalyst bed maintained at 450°, collecting the exit water in fractions, and measuring its $O^{18}$ content by equilibrating with $CO_2$ which was then examined in a mass spectrometer. Experiments also were carried out in which oil was charged to the catalyst simultaneously with the water. In both sets of runs flow rates closely approximated those of commercial operation in which steam and oil are charged to the catalyst. Runs were for a 20-minute period, again conventional for cracking. Typical results are shown in Table I.

TABLE I

OXYGEN EXCHANGE BETWEEN WATER AND SILICA–ALUMINA AT 450°

Catalyst: Houdry Type S-45, 87.5% $SiO_2$–12.5% $Al_2O_3$, $H_2O^{18}$: 1.59 atom % $O^{18}$, normal isotopic concn., 0.20 atom % $O^{18}$.

| Expt. no. | Flow period[a] min. | Oxygen in catalyst, g. | Oxygen in water[a] Charged, g. | Oxygen in water[a] Collected, g. | $O^{18}$ in water fraction, atom % | % Oxygen of oxide in equil. with added $H_2O$[d] |
|---|---|---|---|---|---|---|
| 1 | 10 | 7.87 | 1.29 | | 0.66 | |
| | 10 | | 1.15 | | .91 | Total 44 |
| 2 | 5 | 62.6 | 3.48 | 2.18 | .21 | |
| | | | 3.02 | 2.65 | .24 | |
| | | | 3.11 | 3.15 | .39 | |
| | | | 3.73 | 3.75 | .61 | Total 67[b] |
| 3[c] | 20 | 62.6 | 13.3 | | .60 | 53 |

[a] Values are incremental, not total. [b] In this experiment, 15.0 g. of water was charged during the run—only 13.2 g. was recovered. Averaging the data on a no loss basis disproportionately weights the data toward higher values for % exchange, as is evident from column six. Assuming the 1.8 g. loss showed no exchange, we would arrive at a value of 67% of the oxide oxygen equilibrating. It is reasonable to assume some exchange however, and so the true value for % oxygen equilibrating will be greater than 67%. [c] During this experiment, light East Texas gas oil was simultaneously charged to the catalyst at 1.5 liquid hourly space velocity. [d] For method of calculation see reference 2.

In view of these data, several static experiments were carried out at 450° In these, catalyst and enriched water were sealed into an evacuated tube and heated at 450° for periods of 1.5 to 4.0 hours. Results in all cases indicated that *all* catalyst oxygen had equilibrated. Less exchange was reported previously (ref. 2, Table VIII). The reason for the lower results is not known, although less exchange may occur at the lower water vapor pressures used earlier.

## Discussion

The data of Table I show that one-half or more of the catalyst oxygens exchange in a few minutes, a period in which the characteristic catalyst structure-area, pore-size distribution, does not alter measurably. For extensive loss of area to occur requires months of commercial operation. It should be noted that the figures indicate far more oxygens have exchanged than can be accounted for in the two uppermost surface layers—those together

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[1] T. H. Milliken, G. A. Mills and A. G. Oblad, *Faraday Society Discussions*, **8**, 279 (1950); also Vol. III "Advances in Catalysis," Academic Press, Inc., New York, N. Y., 1951.

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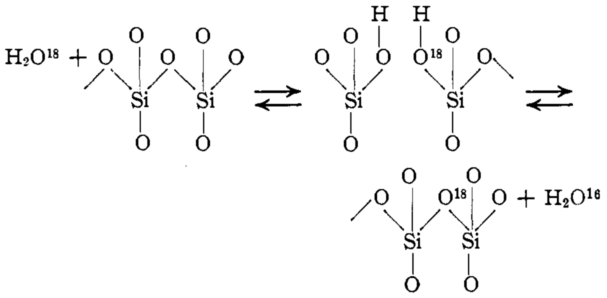
total some 24% of all the oxide oxygens.[2] The exchange of the surface oxygens must be almost instantaneous at 450°. The exchange with surface oxygen seems likely to occur through reversible hydrolysis of metal–oxygen bonds as shown in the equation



For oxygens below the surface the situation is not obvious. With an oxygen defect structure, exchange could occur by oxygen moving into vacant lattice positions, with hole transfer. Silica–alumina catalyst in which the silica presumably has a cristobalite structure is not a semiconductor. However, it does have channels honeycombing the lattice—the diameter of these passages is just large enough to admit an oxygen ion. We believe that at temperatures of ~450° there may be sufficient lattice vibration to allow passage of water molecules (or hydroxyl ions) through this network of channels. It is during this period that the oxygen exchange can occur, with only momentary distortion of the lattice. Such exchange could show a chain-like effect if the incoming oxygen caused a "Walden-type" inversion of the tetrahedron with effects transmitted to adjoining tetrahedra. Further, these channels in which the oxygen molecule moves at high temperature are too small to accommodate a nitrogen molecule, and they are, therefore, not measured by the usual BET method. Polack, Segura and Walden[5] have recently considered oxygen transfer at a catalyst surface and into the interior.

Exchange occurring in this fashion would not necessitate the slow loss of area reported by Ries[6] and Holmes.[7] The silicon ions shown in the equation are bound in a cross-linked structure. For area loss to occur would perhaps require simultaneous hydrolysis of three or four metal–oxygen bonds, allowing the —O—Si(OH)$_3$ to "flop over" to a new position with loss of area.

Perhaps the most important information to be derived from these experiments is the indication of the dynamic nature of the oxide structure. Although the over-all physical structure remains fixed, the high mobility of individual oxygen atoms testifies to the highly dynamic state of equilibrium. This mobility found experimentally in the presence of water indicates clearly that the small shift of oxygen position which was proposed[1] can occur easily.

The catalytic system of silica–alumina with water as co-catalyst is believed to correspond to the aluminum chloride system with hydrogen chloride co-catalyst.

$$HOH + Al(O-)_3 \rightleftharpoons HAl(O-)_4$$

$$HCl + AlCl_3 \rightleftharpoons HAlCl_4$$

Just as HAlCl$_4$ has not been found to exist in the free state,[8] so as stated earlier,[1] we do not believe the acid HAl(O–)$_4$ exists in the free state especially at high temperatures. However, in the presence of a Lewis base, B, for example, nitrogen compounds or olefins, the "salt" of the acid can be stabilized.

$$HOH + B + Al(O^-)_3 \rightleftharpoons BH\ Al(O^-)_4$$

$$HCl + B + AlCl_3 \rightleftharpoons BH\ AlCl_4$$

The formation of the stable salts as depicted involves a "coördination induction" or an "acid induction" through the influence of the silica on the alumina. Such a coördination induction can be likened to the "valence inductivity" described by Selwood.[9] The latter effect, plus "valence oscillation" on the basis of the ideas proposed here, plays an important role in the catalytic action of semiconductor metal oxides and metals. This is described in greater detail by Cook and Oblad.[10] The creation of active sites on catalyst surface by reactants also has been advanced by Taylor and Thon[11] from kinetic data.

Finally, it is of interest to examine the implications of a mobile catalyst surface in connection with problems such as effect of poisons on catalytic behavior. If the surface represents a two dimensional "fluid" acid, then similarities to other acids such as sulfuric and phosphoric become evident. For these homogeneous acids, relatively small amounts of bases such as water or nitrogen compounds are effective poisons. Considering 100% sulfuric acid which will ionize as

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

the presence of water gives rise to the following reaction

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

If the catalytic activity is proportional to the concentration of $(H_3SO_4^+) = K(H_2SO_4)^2/(HSO_4^-)$, then a few per cent. of water or other Lewis bases will reduce the catalytic activity to a very low value, where $K$ equals a small number. For example, since $K(H_2SO_4)^2 = 0.00073$[12] expressed on a molal basis, 1 wt. % water, corresponding to 0.57 molal, will introduce essentially 0.57 molal HSO$_4^-$ and therefore decrease the H$_3$SO$_4^+$ concentration from 0.03 to 0.001, a decrease of 30-fold. This great sensitivity to water "poisoning" has received a more exact treatment employing Hammett's $H_0$ function to relate concentration of acid to catalytic activity.[13] In a like manner, poisoning

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[8] H. C. Brown and H. W. Pearsall, THIS JOURNAL, **73**, 4681 (1951).

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[10] M. A. Cook and A. G. Oblad, *Ind. Eng. Chem.*, **45**, 1456 (1953).

[11] H. A. Taylor and N. Thon, THIS JOURNAL, **74**, 4169 (1952).

[12] L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932).

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experiments with cracking catalysts do not necessarily prove heterogeneity of surface. We do not intend to imply by this that silica–alumina has a homogeneously active surface—there is considerable evidence for heterogeneity, and in theory we should expect such heterogeneity depending on the geometry of the aluminum and silicon atoms in the surface. We wish merely to indicate that by using the concept of the mobility of the surface, poisons need not be present in amounts stoichiometrically equivalent to the total active surface to cause essentially complete deactivation. The surface of cracking catalysts then behaves to a certain degree like a two-dimensional mobile acid.

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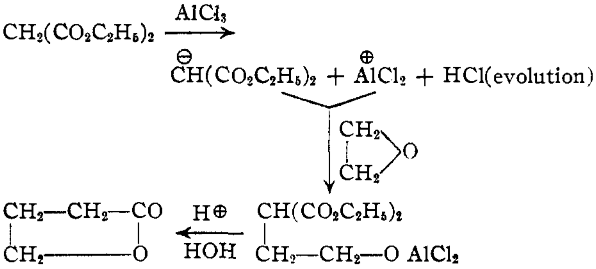
# Alkylation of Malonic Ester by Ethylene Oxide Catalyzed by Anhydrous $AlCl_3$

BY CHITTARANJAN RAHA

RECEIVED DECEMBER 31, 1952

Available methods[1–3,5–14] of synthesis of γ-butyrolactone are not easily workable and give poor yields. A consideration of the mechanism of reaction of ethylene oxide as discussed by Hammett[15] suggested that the alkylation of malonic ester by ethylene oxide in the presence of anhydrous aluminum chloride might be an effective method for the preparation of γ-hydroxy acids. Breslow and Hauser[4] have previously described the alkylation of acetoacetic ester with benzyl chloride in the presence of boron trifluoride.

The present reaction may be explained as



## Experimental

Sixty-four grams (0.4 mole) of malonic ester dissolved in 50 ml. of absolute chloroform was added slowly to 34 g. (0.25 mole) of coarsely powdered anhydrous $AlCl_3$[16] in a 3-necked flask fitted with a reflux condenser, a dropping funnel, an all-glass stirrer and a gas inlet tube. Hydrogen chloride was evolved. Ethylene oxide, generated by dropping 21 g. (0.26 mole) of ethylene chlorohydrin slowly on 20 g. (0.5 mole) of powdered sodium hydroxide under absolute toluene, was passed into the reaction mixture at room temperature with mechanical stirring. The rate of introduction of ethylene oxide was regulated so that the ether refluxed. After addition was complete, the mixture was cautiously acidified with 5 *N* hydrochloric acid, and then refluxed for five hours. The solid which separated on acidification dissolved within a few minutes. The light greenish mixture was then cooled, saturated with salt and extracted with benzene. The benzene extract was washed with a small amount of water, dried over anhydrous sodium sulfate and concentrated. The residual thin liquid was fractionated under reduced pressure.

The yield of γ-butyrolactone obtained as a colorless thin liquid, b.p. 85–110° (11 mm.); 105–120° (15 mm.), was quantitative (based on the ethylene chlorohydrin used).

*Anal.* Calcd. for $C_4H_6O_2$: C, 55.8; H, 6.9; neut. equiv., 86. Found: C, 55.42; H, 7.3; neut. equiv., 84, 86; $n^{35}$ 1.3760.

The liquid γ-lactone which boiled usually over a range could be collected in two distinctly different fractions which had the same contents of carbon and hydrogen and same saponification equivalent. This property is possibly due to a dimorphism as suggested by Sueur.[17]

In one experiment the two fractions were: I, b.p. 85° (11 mm.), 105° (15 mm.), yield 5 g.; II, b.p. 130° (11 mm.), 140° (15 mm.), yield 17 g. In other experiments the relative proportions of the two fractions varied.

In more or less identical yield the two fractions gave a 2,4-dinitrophenylhydrazide, m.p. 93–94°.

*Anal.* Calcd. for $C_{10}H_{12}N_4O_6$: C, 42.26; H, 4.225; N, 19.72. Found: C, 42.48; H, 4.323; N, 19.59.

**Acknowledgment.**—Thanks are due to Dr. D. M. Bose, Director of the Bose Institute, for his encouragement and interest in this work. The author is indebted to Dr. S. K. Mukherjee, Department of Applied Chemistry, for his valuable help.

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(13) Traube and Lehmann, *Ber.*, **32**, 720 (1899); **34**, 1971, 1976 (1901).

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(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., p. 1940, 301.

(16) The yield depends on the freshness of anhydrous $AlCl_3$.

(17) Sueur, *Ann. Rept. Chem. Soc.* (*London*), **9**, 90 (1912).

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# Anhydrous $AlCl_3$-Catalyzed Alkylation of Ethyl Cyanacetate by Ethyl Chloroacetate

BY CHITTARANJAN RAHA

RECEIVED MARCH 23, 1953

Breslow and Hauser[1] have observed that a reactive methylene compound, *e.g.*, acetoacetic ester, can be ar-alphylated by benzyl chloride in the presence of an acid catalyst such as boron trifluoride. A similar reaction, *viz.*, alkylation of cyanoacetic ester by means of ethyl chloroacetate in presence of anhydrous aluminum chloride, has been studied by the present author.

The yield of the alkylated product varied with the amount of catalyst used, but unlike a base-catalyzed reaction even a large amount of the acid catalyst failed to produce in a single step a dicondensation product. The results of comparative runs of experiments carried out in presence of an acidic catalyst and a basic catalyst are tabulated.

## Experimental

**Alkylation of Cyanoacetic Ester with Ethyl α-Chloroacetate to Yield the Monocondensation Product.** Acid Cata-

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