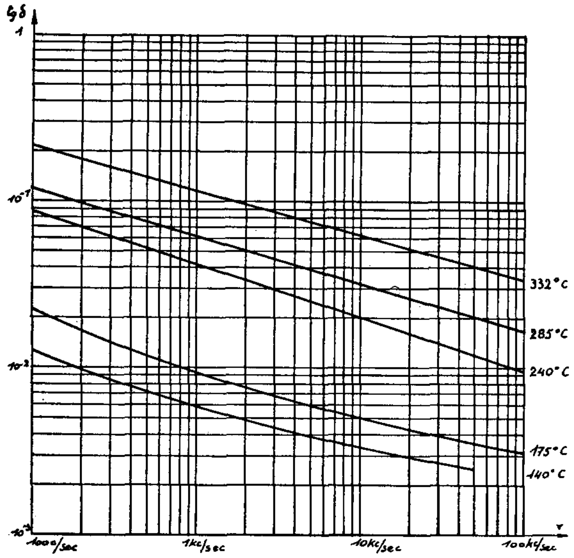

FIG. 2.

of its dielectric properties is quite different. The curves *tgδ versus* frequency at different temperature give no maximum as shown in Fig. 2.

Further investigations are in progress and will be published in a later paper. Measurements are in progress on kaolinites and dickites of different origin in order to see to what factor the observed effects are due.

We wish to thank Professor Dr. W. Dekeyser, who suggested this study, for his interest and encouragement. We also thank I.R.S.I.A. (Brussels) who sponsors the Comité pour l'établissement de la carte des sols et de la végétation de la Belgique.

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# On the Double-Maxima Distribution of Deutero-Paraffins

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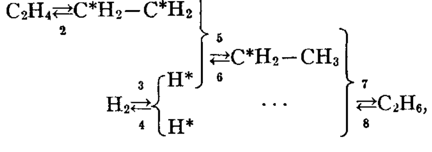
(Received May 14, 1956)

THE distribution of deutero-paraffins in the catalytic deuteration of olefins was found first by Turkevich *et al.*,[1] and its mechanism has been discussed by many authors.[1-3] A new type of distribution with double maxima has further been observed by Bond and Turkevich,[4] who studied the reaction of a mixture having the composition $C_3H_6$, 51.5%; $C_3D_6$, 41.5%, and $C_3HD_5$, 7.0%.

The writer would like to give here an explanation of this particular distribution on the basis of the mechanism[4] formerly proposed by himself to explain the earlier experimental results.

For the sake of simplicity, it will be illustrated for the case of ethylene. The reaction between hydrogen and ethylene takes place with the scheme,



$$\left.\begin{array}{l}\left.\begin{array}{l}\mathrm{C_2H_4}\underset{2}{\overset{1}{\rightleftarrows}}\mathrm{C^*H_2-C^*H_2}\\ \mathrm{H_2}\underset{4}{\overset{3}{\rightleftarrows}}\left\{\begin{array}{l}\mathrm{H^*}\\ \\ \mathrm{H^*}\end{array}\right.\end{array}\right\}\underset{6}{\overset{5}{\rightleftarrows}}\mathrm{C^*H_2-CH_3}\\ \qquad\qquad\qquad\qquad\cdots\end{array}\right\}\underset{8}{\overset{7}{\rightleftarrows}}\mathrm{C_2H_6},$$

where an asterisk denotes a chemisorbed bond. Assuming that the isotopic replacement does not alter the rates of respective reactions $V_i$, the steady-state conditions relating to each intermediate may be stated as follows.

$$\begin{aligned}(2V_4+V_5+V_7)y(\mathrm{D}^*)=V_3[&2y(\mathrm{D}_2)+y(\mathrm{HD})]\\&+V_6[y(\mathrm{C_2D_5}^*)+\cdots+\tfrac{1}{3}y(\mathrm{C_2H_4D}^*)]\\&\qquad+V_8[y(\mathrm{C_2D_6})+\cdots+\tfrac{1}{6}y(\mathrm{C_2H_5D})]\end{aligned}$$

$$(V_2+V_5)y(\mathrm{C_2H_4}^{**})=V_1y(\mathrm{C_2H_4})+V_6[y(\mathrm{C_2H_5}^*)+\tfrac{1}{3}y(\mathrm{C_2H_5D}^*)]$$

$$\begin{aligned}&(V_6+V_7)y(\mathrm{C_2H_5}^*)\\&\qquad=V_5y(\mathrm{H}^*)y(\mathrm{C_2H_4}^{**})+V_8[y(\mathrm{C_2H_6})+\tfrac{1}{6}y(\mathrm{C_2H_5D})],\end{aligned}$$

where $y$ denotes the fraction of each isomer. Putting $y(\mathrm{D_2})=1$, $y(\mathrm{C_2H_4})=y(\mathrm{C_2D_4})=\frac{1}{2}$ in the foregoing equations, and eliminating $y$'s of the intermediates, we have immediately the ratio of the rates of hydrogen formation at the stage of the reaction as follows.

$$\mathrm{H_2}:\mathrm{HD}=V_4y(\mathrm{H}^*)^2:2V_4y(\mathrm{H}^*)y(\mathrm{D}^*)=1:2\Omega,$$
$$\Omega\equiv y(\mathrm{D}^*)/y(\mathrm{H}^*).$$

Assuming further that $V_1\simeq V_2\gg V_i(i=3,4,\cdots,8)$ and $V_8\ll V_7\ll V_6\simeq V_5$, we have similar expressions for ethanes and ethylenes approximately,

$$\text{ethanes};\ d_0:d_1:d_2:d_3:d_4:d_5:d_6\simeq 1:2\Omega:\Omega^2:2R\Omega^2:1+R\Omega^2:2\Omega:\Omega^2$$

$$\text{ethylenes};\ d_1:d_2:d_3\simeq 1:R:1$$

$$\Omega\simeq(6V_3+V_6)/V_6=1+6V_3/V_6>1>R=y(\mathrm{D}^*)V_6/3V_2,\ R\Omega<1.$$

From these relations it follows that the distribution of paraffins has always two maxima at $d_2$ and $d_{N+2}$ if $\Omega\gg 1(V_3\gg V_6)$, or at $d_1$ and $d_{N+1}$ if $\Omega$ is greater than but near to unity $(V_3\ll V_6)$, that hydrogen deuteride predominates over hydrogen, and that the distribution of deutero-olefins has a minimum at $d_{N/2}$. These conclusions may be applicable to the cases of ethylene $(N=4)$, propylene $(N=6)$, and *cis*-2-butene $(N=8)$.

It should be noted that the random distribution[2] could not explain this particular distribution, because it yields always one maximum.

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# Differential Capacitance in Electrolytes

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(Received May 22, 1956)

IN connection with differential capacitance $(C^{(d)})$measurements in a methanol solvent, Grahame[1] recently postulated that the rapid increase observed in $C^{(d)}$ with sufficiently negative potentials, arises from electrostriction which separates charge centroids of the solvent molecule and hence increases the effective dielectric constant of the inner region next to the cathode.

Another explanation,[2] which shows good agreement with experiment for water solvent, is based on the different assumption that the internal field causes solute ions to press against the inner layer and decrease its thickness, with a consequent increase of $C^{(d)}$. This compression is not of major importance until sufficiently negative potentials are reached that dielectric saturation of the solvent molecules in the inner layer is substantially complete. The interplay of diffuse-layer capacitance, dielectric saturation, and inner-layer compression also accounted well for the characteristic maximum of $C^{(d)}$ observed at low solute concentrations in water.[2,3]

Since Grahame's type of electrostriction depends upon the dipole moment of the solvent molecule, which interacts much less strongly with the internal field than do charged ions adjacent the inner layer, we feel that compression caused by the latter will outweight the former's effects. Further, charge-centroid separation might increase the inner layer thickness, at least partly canceling the effect on $C^{(d)}$ of any dielectric constant increase. Grahame's methanol results are qualitatively consistent with the assumption of compression. The more rapid rise of $C^{(d)}$ at appreciable negative potentials in methanol compared to that of water follows on this picture from the three-times-greater compressibility of methanol.

Grahame[1] has suggested that a "natural" electric field which produces partial dielectric saturation in the inner layer may exist at the cathode even at the electrocapillary maximum potential (e.c. max potential) where surface charge density is zero. This idea was originally incorporated in an early version of the author's theory[2] but was eliminated as inconsistent with the quoted equality of the differential and static capacitances at the e.c. max.[4] Professor Grahame has recently made it clear[5] that such equality is only a consequence of the usual assumption of zero natural field at the e.c. max potential when static capacitance is calculated from $C^{(d)}$ measurements.

The author's theory can be readily modified to include a natural field $\epsilon_0$ together with the static internal field $\epsilon_1$ in the expression for dielectric saturation. Since the field appears squared, $\epsilon_1^2$ may be replaced by $(\langle\epsilon_0+\epsilon_1\rangle_{\mathrm{Av}})^2$, $(\langle\epsilon_0^2+\epsilon_1^2\rangle_{\mathrm{Av}})$, or by an intermediate form, where the angular brackets denote a time average. Unless $\langle\epsilon_0\rangle_{\mathrm{Av}}=0$, the first expression would cause a change in the e.c. max potential as Grahame has suggested to explain the methanol results.[1] A nonzero $\langle\epsilon_0\rangle_{\mathrm{Av}}$ would also contribute to layer compression. If $\epsilon_0$ were rapidly oscillating with zero average value, however, the second form would still predict some initial dielectric saturation but no change in e.c. max potential or compression. Also, no applied field could reduce the initial dielectric saturation. For an oscillating field for which $(\langle\epsilon_0^2\rangle_{\mathrm{Av}})^{\frac{1}{2}}>\langle\epsilon_0\rangle_{\mathrm{Av}}>0$, one would expect both a change in e.c. max potential and an initial saturation greater than that produced by $\langle\epsilon_0\rangle_{\mathrm{Av}}$ alone. Experimental evidence indicates that an $\epsilon_0$ of this character may be more important in methanol than in water, where saturation requires higher fields. The differences in compressibility and saturability between these materials and the possible presence of a natural field can probably account for their somewhat different $C^{(d)}$ curves.

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[4] D. C. Grahame, Chem. Revs. **41**, 441 (1947).
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# Formation of Mixed Crystals in the Use of the Alkali-Halide Disk Technique for Preparing Samples of KAu(CN)₂ for Infrared Spectra*

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(Received May 16, 1956)

In the use of the alkali-halide disk technique[1] for observing infrared spectra of solids, there have been reported changes in spectra attributed either to metathesis[2,3] or formation of mixed crystals.[2-4]

Sample disks were prepared by pulverizing 2 mg of $\mathrm{KAu(CN)_2}$ with one gram of optical potassium halide for ten minutes in a high speed vibration mill and pressed *in vacuo* at 55 000 lb (about 170 000 psi) for five minutes. In all cases (KCl, KBr, or KI), two strong bands appeared initially, at 2141 and 427 cm$^{-1}$, the asymmetric C−N and C−Au−C stretching vibrations, respectively.[5] In the KCl disks no change occurred with time. However, with the KBr and KI disks, in a few minutes the intensities of these bands diminish, and two new bands appear at 2154 and 448 cm$^{-1}$. The high-energy bands are shown in Fig. 1. The depletion of 2141 and increase of 2154 appear to be linear with time for an hour or two, when the change becomes slower and finally stops. If the disks are reground and repressed, the reaction continues further until finally we observe only the absorption bands at 2154 and 448 cm$^{-1}$ with about the same absorption coefficient as the original peaks. Most of the reaction occurs after preparation of the sample disk. The amount of pressure (30 000–170 000 psi) makes no appreciable difference in rate or extent of reaction. In mixtures more concentrated in $\mathrm{KAu(CN)_2}$, the reaction cannot be made to go to completion even by warming after repeated regrinding and repressing.

There appear to be three possibilities to consider for the reaction occurring: X = Br or I

(A). $\mathrm{Au(CN)_2^-+X^-=XAu(CN)^-+(CN)^-}$;

(B). $\mathrm{Au(CN)_2^-+}n\mathrm{X^-=Au(CN)_2X}_n^{-(1+n)}$; and

(C). Incorporation of $\mathrm{Au(CN)_2^-}$ into the cubic KX lattice.

Possibility (A) was ruled out by observing the reaction using $\mathrm{KAu(CN)_2}$ enriched to 64 atomic percent in $\mathrm{N^{15}}$. Four peaks appear originally (asymmetric C−N stretching vibrations of $\mathrm{N^{15}C^{12}AuC^{12}N^{15}}$ and $\mathrm{N^{14}C^{12}AuC^{12}N^{14}}$ at 2110 and 2141 cm$^{-1}$, respectively, and the two C−N stretching vibrations of $\mathrm{N^{15}C^{12}AuC^{12}N^{14}}$ at 2117.5 and 2153 cm$^{-1}$). These peaks disappear, and four new peaks appear at 2120.5, 2129, 2154, and 2164 cm$^{-1}$. If $\mathrm{BrAuCN^-}$ were the reaction product, only two CN stretching frequencies would appear. It cannot be a mixture of $\mathrm{Br_2Au(CN)^-}$ and $\mathrm{BrAu(CN)^-}$ as only one peak is infrared active in the reaction product of $\mathrm{N^{14}C^{12}AuC^{12}N^{14}}$. Further evidence against possibility (A) is the lack of appearance of a KCN peak. Such a peak was observed in a KBr disk having an equivalent amount of KCN.

The second possibility is unlikely because the extinction coefficient of the reaction product is about the same as that of the original species. One would expect that if an ion of greater negative charge were formed, the extinction coefficient would increase considerably as is the case with the silver-cyanide and cuprocyanide complexes.[6]

This leaves reaction (C) as most probable. Solid $\mathrm{KAu(CN)_2}$ is normally rhombohedral. Apparently the linear $\mathrm{N-C-Au-C-N^-}$

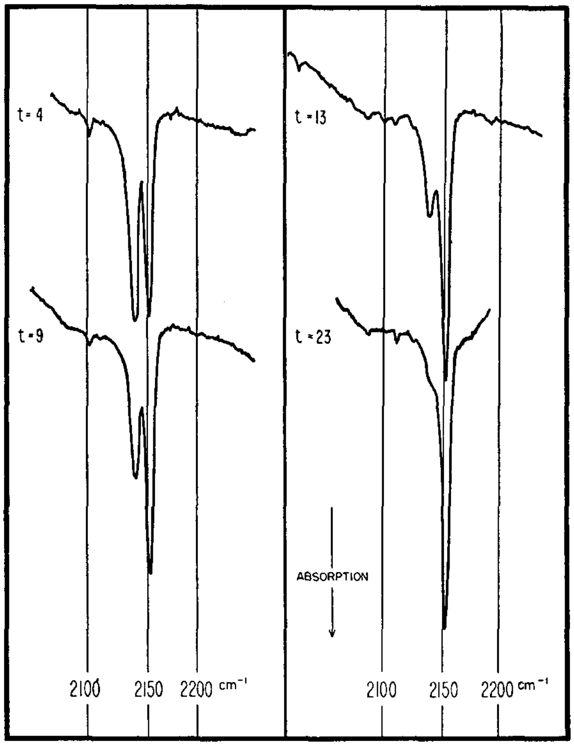

Fig. 1. Asymmetric C−N stretching frequency of $\mathrm{Au(CN)_2^-}$ for solid $\mathrm{KAu(CN)_2}$ in KBr (about 0.2% $\mathrm{KAu(CN)_2}$ by weight). This sample was ground for 11 min, pressed, reground for 13 min, and represssed. $t$ = minutes after second pressing.