curves when these values are substituted into Eq. (1) are shown in Fig. 1. It will be seen that the changes in the concentrations of methylcyclohexanones obtained experimentally are in good agreement with those given by the equations, especially for o- and m-cresols, throughout the course of hydrogenation. From the value of K and the ratio of the rate constants of methylcyclohexanone and cresol, $k_2/(k_1 + k_3)$,* the ratio of the adsorption coefficients of the ketone and cresol, b_2/b_1, can be calculated, which is also included in Table 1. It will be seen that the small value of K for o-cresol is mostly due to the kinetic factor, rather than to the difference in the strength of adsorption between o-cresol and 2-methylcyclohexanone.

When the yields of the ketone intermediates obtained by the present kinetic method are compared with those obtained previously by the stereochemistry of the hydrogenation and by the extrapolation of the yield of the ketone versus saturated alcohol to the initiation (see Table 1), it will be seen that, in general, differences in the results are not great and the yields of the ketone intermediates lie mostly between 50% and 65%. It is noteworthy that the yields of 2-methylcyclohexanone estimated by the three methods are all closely consistent with each other, as was expected, since the rate of the hydrogenation of 2-methylcyclohexanone was very small

* These were obtained from the initial rates of hydrogenation of methylcyclohexanone and cresol, respectively, under the same conditions.

and the three methods of estimation could all be applied more accurately in this case.[1]

It is of interest that the yields of the ketone intermediates are nearly the same for three isomeric cresols. This may suggest that the steric factor does not concern with the steps which determine the yields of the ketones and seems also to be in line with the assumption made previously that all kinds of dihydrocresols are produced in equal probability (1).

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[1] The yields of the ketone intermediate obtained by the initial yield method are too small for m-cresol and too great for p-cresol. One reason for this may be that the method is concerned only with the initial states of hydrogenation which may not always be alike with the subsequent states of hydrogenation.

The Migration of Metal Ions in Zeolite-Y as Revealed by ESR of Cu²⁺

The zeolite used in this investigation was a zeolite of type Y with a unit cell composition according to $Na_{56}(AlO_2)_{56}(SiO_2)_{112}\cdot196$ H_2O. Prior to introduction of Cu^{2+} the zeolite samples were ion-exchanged with Mg^{2+}, Zn^{2+}, or La^{3+}. Representative numbers are 18 Mg^{2+}, 12 Zn^{2+}, and 13 La^{3+} per unit cell. The number of copper ions amounts to 0.3 per unit cell. Dehydration was carried out in air or oxygen: 8 hr at 110°C in air, 8 hr at 200°C
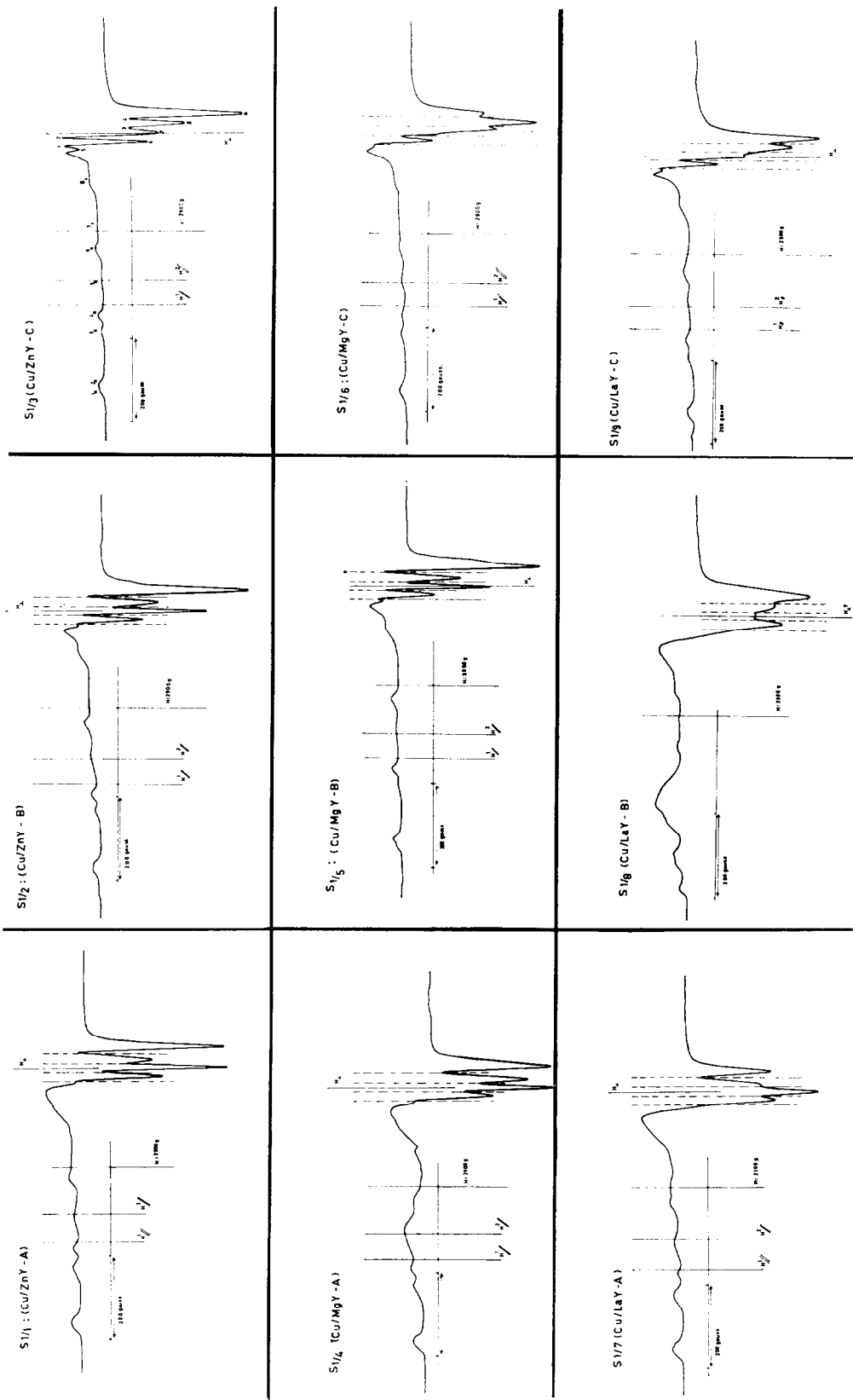
FIG. 1. ESR spectra of the Cu^{2+}-containing zeolite samples. Dehydration temperatures:; B, 2 A, 110°00°; C, 400°C.

in air, and 72 hr at 400°C in oxygen. Thermogravimetry indicated the presence of 1.1% residual water in the latter case. Metal ions in the samples were determined after destruction of the zeolite by hot concentrated hydrofluoric acid. Conventional methods were applied for the quantitative analysis of the metal ions.

The ESR spectra of Cu^{2+} in the various cases all show axial symmetry, with an exception, perhaps, in spectrum S1/8. They exhibit a well-developed hyperfine structure in the parallel and perpendicular directions, due to the copper nucleus with $I = \frac{3}{2}$. The g anisotropy is sufficiently large to separate the parallel and perpendicular bands. The complete ESR spectra of Cu/Mg-Y, Cu/Zn-Y, and Cu/La-Y shown in Fig. 1; A, B, and C refer to dehydration temperatures of, respectively, 110°, 200°, and 400°C.

On the low-field side of the spectra two groups of four equidistant signals each can in all cases but one (S1/8) be recognized. This is not possible on the high-field side (perpendicular band), presumably because $A_\perp \ll A_\parallel$. These four signals are not equidistant, due to strong overlapping of the two assumed groups of signals.

The low-field regions of the spectra appear on a larger scale in Fig. 2a-i, in the same order as in Fig. 1. Discerning the two groups of signals by numbers 1 and 2, the numerical data of the spectra are combined into Table 1.

The relative intensities of the low-field components were estimated graphically and are qualitatively compared in Table 2.

Although the structures of zeolites were the subject of many investigations (1–9), little is still known about the behavior of cations such as those used in the present work. Richardson (10) recently published on Cu^{2+} in zeolite on the basis of earlier work by Nicula et al. (11) on the dehydration of Cu-Na-Y-zeolite. A certain amount of speculation remains inherent in the interpretation. To avoid this we made no attempts to specify the cation sites we need for the interpretation of our experimental data.

The entries in Table 1 present a rather peculiar situation. The g values vary only slightly from sample to sample (accuracy
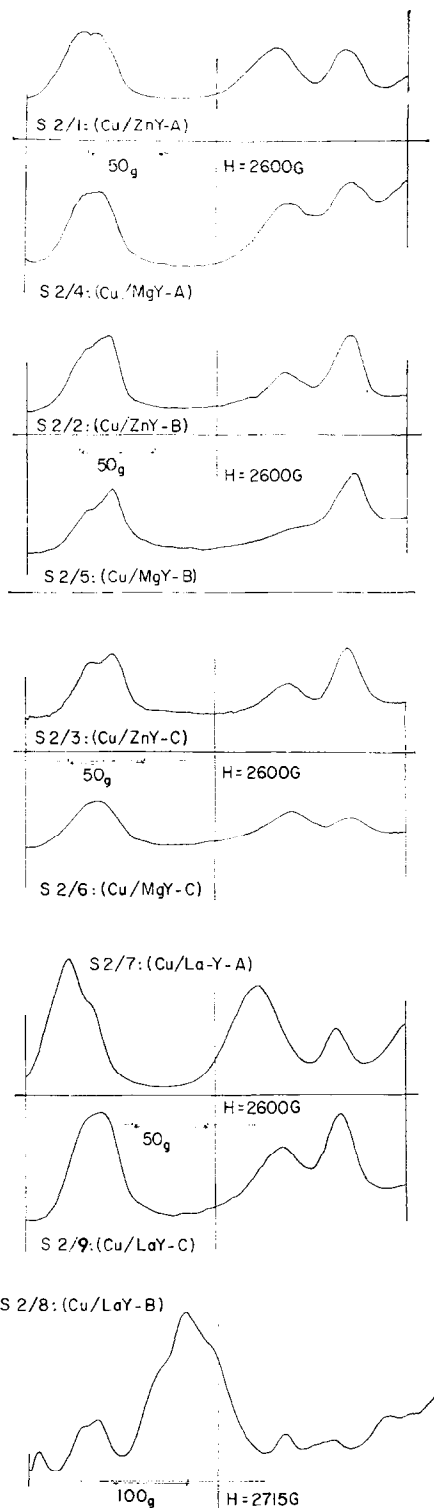

FIG. 2. Parallel band of the spectra from Fig. 1.

TABLE 1
ESR PARAMETERS OF ZEOLITE SAMPLES[a]

		$A_{\|1}$	$A_{\|2}$	$A_\perp$	$g_{\|1}$	$g_{\|2}$	$g_\perp$
Cu/ZnY-A	S1/1	129	160	20.5	2.383	2.323	2.064
Cu/ZnY-B	S1/2	129	160	20.5	2.381	2.328	2.064
Cu/ZnY-C	S1/3	129	160	20.5	2.377	2.325	2.062
Cu/MgY-A	S1/4	129	160	20.5	2.377	2.322	2.061
Cu/MgY-B	S1/5	129	160	20.5	2.375	2.326	2.062
Cu/MgY-C	S1/6	129	160	20.5	2.375	2.326	2.056
Cu/LaY-A	S1/7	131	160	20.5	2.397	2.333	2.067
Cu/LaY-B	S1/8	x	x	x	x	x	x
Cu/LaY-C	S1/9	131	160	20.5	2.378	2.333	2.063

[a] H and A values in gauss; x, not interpreted; $g_\perp$ is no true $g_\perp$, but indicates the center of the perpendicular signal.

$\approx \pm 0.005$) and the hyperfine splittings are essentially constant as a function of temperature. However, in this temperature region dehydration is supposed to occur.

The values of the parameters reported here are fairly close to those reported by Krüerke and Jung (12).

We are inclined to consider the ESR parameters as constants, allowing for minor modifications by second order effects. The signal intensity is then the only remaining variable. To explain this fact we may choose one of two possibilities: either the copper ions enter the zeolite fully hydrated and retain their coördinated water throughout the dehydration, or they are, be it partially or completely, dehydrated during the treatment on 110°C and then persist in that particular state. In view of, for instance, the dehydration of $CuSO_4 \cdot 5H_2O$ the latter possibility seems more appropriate, the more so

TABLE 2
RELATIVE INTENSITIES OF ESR SIGNALS
OF THE PARALLEL BAND[a]

Spectrum	Sample	Relative intensities
S2/1	Cu/ZnY-A	$I_{\|1} \approx I_{\|2}$
S2/2	Cu/ZnY-B	$I_{\|1} < I_{\|2}$
S2/3	Cu/ZnY-C	$I_{\|1} \ll I_{\|2}$
S2/4	Cu/MgY-A	$I_{\|1} \approx I_{\|2}$
S2/5	Cu/MgY-B	$I_{\|1} \ll I_{\|2}$
S2/6	Cu/MgY-C	$I_{\|1} > I_{\|2}$
S2/7	Cu/LaY-A	$I_{\|1} \gg I_{\|2}$
S2/8	Cu/LaY-B	$I_{\|1} ? I_{\|2}?$
S2/9	Cu/LaY-C	$I_{\|1} < I_{\|2}$

[a] $I_{\|1,2}$ is intensity of parallel ESR signal; spectrum S2/8 has not been interpreted.

since the g values differ appreciably from those of hexahydrated copper ions. The difference between $g_{\|1}$ and $g_{\|2}$ must then be caused by the bonding to the two sites 1 and 2. There is no initial preference for either site in the samples Cu/Zn-YA and Cu/Mg-YA (S2/1; S2/4). Gentle dehydration, presumably of ions other than Cu^{2+}, makes site 1 more attractive for both Zn^{2+} and Mg^{2+}, which appear to expel copper ions from that site (S2/2; S2/5). A reason may be that site 1 has fewer ligand ions available than site 2, and since the Mg and Zn ions certainly lost a fraction of their water shell, site 1 is the better substitute. As soon as a major part of the hydrate water is gone the Mg^{2+} tends to occupy the site offering the higher coordination number, i.e., site 2, expelling Cu^{2+} to site 1 (S2/6). Mg usually prefers hexacoordination as in MgO.

Zn^{2+}, preferring lower coordination (cf. ZnO), will upon progressing dehydration tend to occupy site 1, expelling copper to site 2 (S2/3). With La^{3+} present the situation is apparently different. These La ions could, perhaps, remain unaffected even by a heat treatment on 400°C. In that case there would be no reason for it to migrate. The size of the hydrated lanthanum ion, however, may be an important factor in choosing a definite site (S2/7). Spectrum S2/8, which must result from a rearrangement of the ions involved, indicated a situation with at least three sites occupied by Cu^{2+} ions, leading eventually to the simpler S2/9.

We see no obvious explanation of these

phenomena in connection with La^{3+} on the basis of the available data. The conclusion should be that the migration of copper ions is imposed by the migration of the majority cations to favorable, yet unidentified, sites.

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