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NOTE

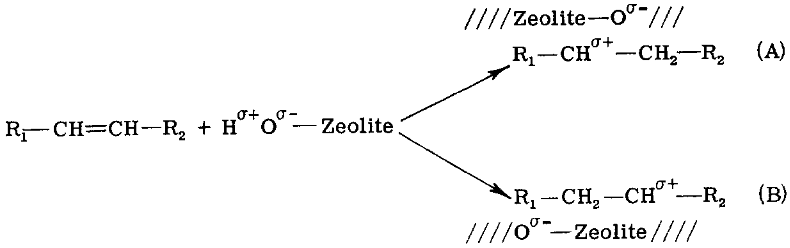
On the ESR Spectra of Adsorbed Olefins on Zeolite Y

Hirschler *et al.* (*1*) have obtained resolved ESR spectra of adsorbed olefins on rare-earth Y zeolite (ReY). To explain the experimental value of the hyperfine splitting (hfs) constant, they considered the electron delocalization over two carbon atoms. To account for the experimental number of hfs components, several different mechanisms of adsorption have been proposed, e.g., (a) stabilization of monomer on zeolite; (b) hydride ion addition and abstraction; and (c) hydrogen atom addition. None of these mechanisms was considered satisfactory by the authors of (*1*).

In this paper we try to support the assumption that a hydrogen atom is added to the molecule, forming a partially charged adsorbed species.

The active center in adsorption results from the reaction between the rare-earth ions and water. Unlike other authors (*2*), we suppose this center to be provided with partial charges ($\sigma+$, $\sigma-$), so that the adsorption center takes the form: $H^{\sigma+}O^{\sigma-}$-Zeolite, where $0 \leq \sigma \leq 1$ and the oxygen is bonded to silicon.

The adsorption of the olefin on a center of this type can be imagined to occur according to the mechanism:*



$$R_1\text{—}CH\text{=}CH\text{—}R_2 + H^{\sigma+}O^{\sigma-}\text{—Zeolite} \rightarrow \begin{cases} \text{////Zeolite—}O^{\sigma-}\text{///} \\ R_1\text{—}CH^{\sigma+}\text{—}CH_2\text{—}R_2 \quad (A) \\ R_1\text{—}CH_2\text{—}CH^{\sigma+}\text{—}R_2 \quad (B) \\ \text{////}O^{\sigma-}\text{—Zeolite////} \end{cases} \qquad (1)$$

The number of experimental hfs components can be correlated with the number of protons (considered equivalent) of the hypothetical adsorbed species [mechanism (1), A or B] obtained by addition of a hydrogen atom to one of the carbon atoms of the double bond.

To support the assumption of partial charges, the experimental hfs constants of the studied olefins have been compared qualitatively with those of some aliphatic radicals adsorbed on an inert layer (*4*) (the electron is not shared with the layer) and quantitatively with aliphatic radicals obtained by radiolysis of solid hydrocarbons (*5*). The hfs constants of reported aliphatic radicals (*5*) are about 25 G. For adsorbed olefins the hfs constants are much smaller (about 13 G, see Table 1) which could result from a lowered free electron density to carbon atom.

It seems that one of the proposed species [for example A, in mechanism (1)] has a lower energy than the other (for example B) and that it is stabilized by adsorption. One can consider that the well-known inequality $E_{C^+\ tert} \leq E_{C^+\text{-sec}} \leq E_{C_+\text{-prim}}$ holds also for the partial charges. In the case of poorly resolved spectra (e.g., octene-1; 2-methyl butene-2) one may emphasize these energetic considerations to explain some disagreement between experimental and

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* The data on the products of olefin isomerization reactions suggest a similar mechanism, in which integral charges are considered (*3*).

TABLE 1
ESR Characteristics of Adsorbed Olefins on ReY

Hydrocarbon	No. of hfs components Exp.	No. of hfs components Theor.	Hfs constant (gauss)	ρ^a	Observations
Pentene-2	7	(A) 7	13.5	0.456	Well resolved spectrum.[b]
		(B) 6	—	—	
2-Methylbutene-2	7	(A) 9	—	—	Poorly resolved spectrum; (A) more stable (the charge on C_{tert})[b]
		(B) 6	—	—	
Hexene-2	7	(A) 7	13.0	0.484	Well resolved spectrum.[c]
		(B) 6	—	—	
4-Methylpentene-2	5	(A) 7	—	—	Poorly resolved spectrum; (B) more stable (the inductive effect of methyl)[b]
		(B) 5	—	—	
Octene-1	5	(A) 5	—	—	Partially resolved spectrum; (B) more stable (the charge on C_{sec})[b]
		(B) 7	12.0	—[d]	

[a] ρ = (hfs constant of adsorbed olefin/hfs constant of aliphatic radical), where the hfs constant of the aliphatic radical is taken as in Ref. (*5*), e.g., 29.6 G for CH_3–$\dot{C}H$–CH_2–CH_2–CH_3 and 26.8 G for CH_3–$\dot{C}H$–CH_2–CH_2–CH_2–CH_3.

[b] Hydrocarbons studied by Hirschler *et al.* (*1*).

[c] Hydrocarbon studied by us, in the same conditions as those of Ref (*1*).

[d] For the hfs constant of this aliphatic radical, one must consider a lower value than for the radicals considered before, but no value could be found in the literature.

hypothetical spectra (A or B, Table 1) and to discriminate between them. Similarly, the methyl inductive effect for the cross-linked hydrocarbons (4-methyl pentene-2, see Table 1) should be taken into account.

The adsorption center formed by oxygen and silicon has not the nuclear magnetic moment necessary to give a hfs component in the ESR spectra.

In conclusion, its seems that the adsorbed olefinic species formed by addition of the hydrogen atom is a *partially charged* carbonium ion. If one considers it as a radical, then the value of the factor ρ calculated in Table 1 can be regarded as representing the value of the partial charge of the adsorbed species.

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