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CATALYSIS OF CIS-TRANS ISOMERIZATION

BY PARAMAGNETIC SUBSTANCES

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Since magnetic spin-spin and "spin of one electron-orbit of another" interactions are weaker than the here already small spin of one electron-orbit of the same electron interactions, it is doubtful that magnetic interactions are responsible for the catalysis of isomerization. The following is a qualitative explanation for the catalytic activity of paramagnetic substances.

If, for example, a doublet electronic state of a catalyst atom interacts with the S and T states of the isomer, two doublet states are formed (D and D* in Fig. 1-b) together with a quartet state. The minimum separation of these doublet states, $\xi$ in Fig. 1-b, will in general be determined by the strength of the chemical binding between catalyst and isomer. Since $\xi$ need only be of the order of $kT$ to make isomerization by path (1') about $10^4$ - $10^7$ times more probable than path (1), it appears that even weak catalyst-isomer interactions can account for the catalytic effect of paramagnetic molecules. Analogous considerations apply to catalysts in triplet states. No corresponding mechanism exists for catalysis of isomerization by substances in singlet states. These conclusions may represent an improvement over the well-known chemical arguments that some atoms (e.g., iodine) catalyze isomerization by binding to an olefinic molecule and "breaking" the carbon-carbon double bond.


3 Specific isomerization rate (soc$^{-1}$) = A exp.(-E/RT).

The energies \( \epsilon \) and \( \epsilon' \) are exaggerated in Fig. 1 for clarity.


SOME ERRATA

Page 4, line 4. Substitute: "Lapworth"

Page 5, last line. Add: ", or radicals."

Page 6, line 2. Should read: "between 0 and co,"

Page 6, line 8. Should not read "of", but: "of"

Page 10, line 19. Should read: "self-explanatory"

Page 18, Remark B4. Should read: "all neutral bases D"

Page 25, Section 9. H2O + CO2 should be listed under n + kπd

Page 27, line 7 in Section 14. Should read: "bπ, hσ and bπ, kσ"

Page 34, line 3 of footnote u. Should read: "Section IV"

Page 34, last line of footnote v. Should read: "Section IV"

Page 36, lines 5-7. Should read everywhere "D" instead of "B"

Page 40, line 23. After "should be polarized", insert "with a large component"

Page 45, line 8. Should read: "u or c"

Page 49, line 1. Should read: "H2O+"

Page 50, next to last line. Should read: "R+ + YQn+1 -"

Page 57, first line. Transpose "inner" and "outer"

Page 59, line 11. Should read: "Walker"