



Remarks on Nitric Oxide Catalyzed CisTrans Isomerization of Dideuteroethylene Harden M. McConnell

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There are two possible interpretations of the observed activation energy. First, if the considerations of the first paragraph apply, then although various detailed kinetic mechanism schemes which fit the kinetics may be formulated, one concludes that the observed activation energy is closely related to the true energy of "crossing" of the N and T states of ethylene; so that, in any case, $E_{T'} < 30$ kcal (1.3 ev). This number is appreciably less than that deduced from the various estimates and calculations of the difference, $E_{N'}-E_{T'}$, which have been given (<15 kcal).⁴

A second possibility is that there is strong $(\gg kT)$ catalystsubstrate interaction³ (chemical catalysis); in fact, in conventional chemical terms, it is quite probable that the mechanism of isomerization involves addition to the double bond with formation of an intermediate unstable radical. The energetics of such a process, so far as known, are consistent with the measured activation energy, while this mechanism yields a calculated entropy factor in reasonable agreement with experiment. In this case, no direct information is gained from our experiments regarding $E_{T'}$.

In the most meticulously studied cases in the literature of catalytic cis-trans isomerization of olefins, namely iodine (bromine) atom catalysis,5 there seems little doubt from the magnitudes of the experimental parameters that very strong atom-substrate interaction is also involved,³ in short, addition to the double bond. It may be remarked that it is doubtful whether physical catalysis of cis-trans isomerization has ever been demonstrated experimentally.6

It is hoped to extend this work to other olefins and catalytic agents.

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Remarks on Nitric Oxide Catalyzed Cis-Trans **Isomerization of Dideuteroethylene**

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N the preceeding letter Rabinovitch and Looney¹ (RL) report an experimental activation energy, $E_c = 27.5$ kcal mole⁻¹, for the NO catalyzed isomerization of trans-ethylene- d_2 . An earlier study² yielded a value of 65 kcal mole⁻¹ for the noncatalyzed activation energy which is identified with the lowest singlet state energy of *perp.*-ethylene, $E_{N'}$. RL have also cited various theoretical estimates3 that the lowest triplet state energy of perp .ethylene, E_T' , is $\gtrsim 50$ kcal mole⁻¹.

We proposed earlier⁴ that the Magee, Shand, and Eyring⁵ (lowenergy)-(low-frequency factor) singlet-triplet isomerization mechanism could be catalyzed by "paramagnetic substances" even though the catalyst-isomer interaction energies were small. This "first-order" theory would put $E_c \approx E_{T'}$. The experimental results and arguments put forth by RL, together with the older studies on iodine catalyzed olefin isomerization, do suggest that many similar catalyst-olefin interactions will involve energies much larger than the lower limits $(\geq kT)$ considered earlier⁴ as being adequate to circumvent the singlet-triplet interconversion problem. Nevertheless, our general energy level scheme,4 and especially the quantummechanical repulsion of the two doublet states, D and D', retain their validity for describing and interpreting the course of isomerization catalysis irrespective of the strength of the catalystisomer interaction. However, for strong interactions, the D-D'

repulsion may amount to, say, 20 kcal mole⁻¹ and may be regarded as effectively "breaking" the carbon-carbon double bond. This seems to be the case for the NO catalysis.

We also wish to use the present note to clarify, and modify, other possibly confusing points in connection with our earlier proposal. First, it must be emphasized that the proposed catalytic mechanism requires the repulsion of two doublet electronic states, D and D', and that, in turn, this repulsion requires electron exchange coupling (i.e., bonding) between catalyst and olefin. Isomerization might also be brought about by strong "ionic" catalysts but the mechanism would be entirely different from that considered herein the ionic case, singlets and triplets would still be distinct. One of the basic requirements invoked for the catalyst is a nonzero electron spin multiplicity and not paramagnetism. Accordingly, both magnetic and nonmagnetic NO molecules ($2\pi_1$ and $2\pi_1$ states) are probably almost equally efficient isomerization catalysts. It must also be recognized that substances in singlet states could serve similarly as catalysts if they have low-lying electronic states of higher multiplicity.

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Ozone Theory in the Troposphere*

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PRESENT theories of ozone formation are based on a photochemical production of ozone in the stratosphere. The resulting vertical ozone distributions agree in general with those measured in the stratosphere but do not agree with ozone measurements in the troposphere. It can be shown that in addition to the ozone produced in the stratosphere large amounts of ozone are also produced in the troposphere and more particularly near the ground. Measured ozone distributions are, therefore, the result of the added effects of stratospheric and tropospheric ozone sources.

It has been shown¹ that ozone can be produced photochemically in an atmosphere with small concentrations of nitrogen dioxide and hydrocarbons. Using mathematical models of urban pollution² one can determine the ozone concentrations produced in an industrial area. Under certain meteorological conditions a cloud of ozone can accumulate over a large area and then move with the wind. The total vertical amount of ozone accumulated in such a cloud, e.g. Los Angeles County, reaches 0.05 mm (SPT) of ozone and more. Tropospheric ozone may be formed by various sources including natural and industrial sources. The world production of tropospheric ozone can be evaluated and the resulting vertical ozone distribution estimated. The ozone concentrations at ground levels due to tropospheric sources are of the order of magnitude of those measured in the lower troposphere. The vertical ozone distribution resulting from the contributions of tropospheric ozone and of stratospheric ozone have been estimated for various general meteorological conditions. Several former inconsistencies between experimental and theoretical results in the troposphere seem to be explained. The latitudinal and seasonal ozone variations were reexamined and the correlation between meteorological conditions and ozone measurements justified.

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