The C–S bond in I is found to be much longer than those in II, tetrahydrothiophene[10] (1.839 ± 0.002 Å), or dimethyl sulfide[11] (1.802 ± 0.002 Å); *i.e.*, I > II ≈ tetrahydrothiophene > dimethyl sulfide. The C–S–C angle in I is smaller than that in II by as much as 10° and contrasts with the corresponding angles in tetrahydrothiophene (93.4 ± 0.5°) and dimethyl sulfide (98.9 ± 0.2°); *i.e.*, I < II < tetrahydrothiophene < dimethyl sulfide. Analogous trends have been observed in the related hydrocarbons bicyclo[2.1.1]-hexane[12], norbornane,[9,13] cyclopentane,[14] and propane,[15] where the carbon valence angles corresponding to the above C–S–C angles are 85.4, 93.1 (or somewhat larger[13]), 102–106 (pseudorotation), and 112.4°, respectively.

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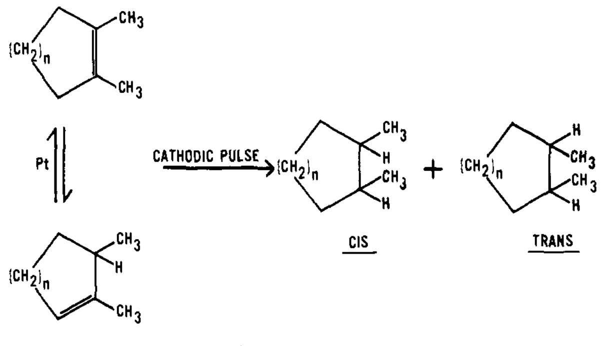
Molecular Rearrangement of a Cyclic Olefin at a Fuel Cell Electrode

Sir:

While investigating the adsorption and reactions of various cyclic olefins at fuel cell electrodes, a molecular rearrangement has been observed involving a one-carbon ring expansion of a dimethyl-substituted cyclopentene.

The products expected from cathodically pulsing an electrocatalyst upon which a 1,2-dimethylcycloolefin has been adsorbed are the corresponding *cis*- and *trans*-1,2-dimethylcycloalkanes.[1] These products have been obtained under heterogeneous catalysis conditions for both dimethylcyclopentene[2,3] and dimethylcyclohexene,[3,4] and under conditions of electrocatalysis for dimethylcyclohexene.[5] Although both *cis*- and *trans*-1,2-dimethylcyclopentane are obtained on cathodically pulsing an electrocatalyst which has been in contact with 1,2-dimethylcyclopentene,[5] a competing reaction, highly dependent upon adsorption potential, has been observed.



The experimental apparatus has been described previously.[6] The working electrode was an LAA25 American Cyanamid type consisting of 25 mg/cm² of platinum black bonded with 25% Teflon on a tantalum screen and having a geometrical area of 20.2 cm². The electrolyte, 85% H_3PO_4, was maintained at 120° and contact to the reference electrode compartment was effected through a Luggin capillary. Water vapor losses from the electrolyte, due to the elevated working temperature, were replenished by passing humidified inert gas into the cell. The humidifier was kept at 69–70°, thus equalizing the water vapor pressure in both humidifier and cell. Potentials were measured against the dynamic hydrogen electrode[7] which was typically 40 mV cathodic to the normal hydrogen electrode in the same electrolyte. The working electrode potentials were controlled by a Wenking 66TS3 potentiostat monitored with a Keithley 610B electrometer, and galvanostatic pulses were obtained with a Kepco CK8-5M power supply.

A potential-step technique was used to prepare a reproducible catalyst surface.[8,9] The working electrode was initially held at 1.35 V under oxygen-free helium until the observed current had decreased to 10 mA to oxidize any adsorbed impurities. The potential was then decreased to 0.05 V for 20 min to reduce the oxide film. The electrode was then set at the adsorption potential and the hydrocarbon passed over the electrode in a helium carrier gas at a flow rate of 1.4×10^{-6} mol/min. Steady state was achieved in approximately 1 hr, after which reactant olefin was swept from the lines with helium. Cathodic pulsing of the electrode at a current of 1.0 A desorbed the hydrocarbons which were then trapped in chromatoquality *n*-octane.

Product separation and identification were accomplished with a 5750 Hewlett Packard gas chromatograph on a 20-ft Carbowax column at 81°, or with a Perkin-Elmer Model 154D vapor fractometer employing a 6-ft squalane column at various temperatures from 62 to 120°. The reactant olefin (K and K Laboratories) was determined to be 99% pure, with the major impurities being isomeric species. The absence of any six-membered-ring compounds, both saturated and unsaturated, in the reactant was verified by gas chromatography.

cis- and *trans*-1,2-dimethylcyclopentane were the principal products obtained upon cathodically desorbing hydrocarbons from a fuel cell electrode which had been maintained at 0.30 V during contact with 1,2-dimethylcyclopentene. 1,2-Dimethylcyclopentene isomerizes during adsorption to give an equilibrium mix-

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[1] On passing a 1,2-dimethylcycloolefin over the electrocatalyst, an equilibrium is established between the 1,2- and 2,3-dimethylcycloolefins. Thus the *cis*- and *trans*-dimethylcycloalkanes produced are the result of cathodically pulsing an electrode which has been in contact with an equilibrium mixture of isomeric olefins.

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ture of 1,2- and 2,3-dimethylcyclopentene. This equilibrium, consisting of seven times as much 1,2-dimethylcyclopentene as 2,3-dimethylcyclopentene, was observed with or without a potential applied to the working electrode, and was obtained with either cycloolefin as reactant. On raising the adsorption potential to 0.50 V, however, gas chromatographic analysis of the desorbed products revealed compounds with retention times corresponding to those of cyclohexane and methylcyclohexane along with the expected *cis*- and *trans*-1,2-dimethylcyclopentanes.

The correspondence of retention times of the pulse products with cyclohexane and methylcyclohexane knowns on two dissimilar column materials (Table I) indicates that the pulse products and the knowns are identical. A typical run produces approximately 2.8×10^{-3} mmol of total pulse products, of which between 18 and 24% are six-membered-ring compounds. Cyclohexane accounts for about 60% of the cyclohexyl products. Demethylation of adsorbed cyclic olefins has been observed to occur under similar conditions[5] and probably accounts for the observation of cyclohexane. The inability to detect cyclohexane or methylcyclohexane in the products from the 0.30-V adsorption potential or on passing the olefin over the electrode at 0.05 V indicates that the rearrangement takes place as a result of the more anodic adsorption potential and is not a consequence of the cathodic pulse, since the pulse is independent of adsorption potential. If the rearrangement were a result of the pulse, cyclohexyl products should be seen after all adsorption potentials. Likewise, the rearrangement cannot be simply a consequence of the temperature and electrolyte acidity, or again cyclohexyl products should be seen from all potentials or even without an imposed potential.

Table I. Comparison of Retention Times of Cyclohexane and Methylcyclohexane with Pulse Products of 1,2-Dimethylcyclopentene Adsorption

	Squalane, 91°	Squalane, 62°	Carbowax, 81°
Cyclohexane	4 min, 05 sec	6 min, 57 sec	4 min, 21 sec[a]
Pulse product	4 min, 05 sec	6 min, 57 sec	4 min, 21 sec[a]
Methylcyclohexane	6 min, 42 sec	12 min, 03 sec	*b*
Pulse product	6 min, 42 sec	12 min, 03 sec	*b*

[a] Occurs as a shoulder on the *trans*-dimethylcyclopentane peak.
[b] Occurs under the *cis*-dimethylcyclopentane peak.

There are numerous examples of cyclopentyl ring expansions in strong Lewis acids[10] and under catalytic dehydrogenation[11] and hydrogenolysis.[12] However, to our knowledge, this is the first example of a hydrocarbon ring expansion which occurs on a platinum black electrode. The previously observed electrochemical similarities of cyclohexyl systems[5,13] to aromatics suggest that attainment of an aromatic π-adsorbed intermediate may provide the driving force for this rearrangement.

Further work is in progress on the mechanism of this ring expansion.

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An Activation Energy in the Quenching of a Triplet State

Sir:

Electronically excited states can be deactivated not only by unimolecular paths but also by quenching collisions with other compounds. The quenching process can involve energy transfer or a chemical interaction (with or without formation of a stable product), and both processes have been invoked in the photochemistry of ketones.[1–7]

Usually studies of photochemical quenching have been restricted to systems at a fixed temperature, and generally the kinetics have been interpreted on the basis of rate constants at room temperature. However, we have recently reported[8] lifetimes for the triplet state of 2,3-pentanedione in the gas phase at temperatures between 25 and 90° which allow a study of the temperature dependence of the quenching ability of added compounds. In this preliminary communication, we report preexponential factors and activation energies for the quenching of the triplet state of 2,3-pentanedione by acrolein, crotonaldehyde, and methyl vinyl ketone.

2,3-Pentanedione in the gas phase (concentrations in the range $5\text{–}20 \times 10^{-4}\ M$) was excited by a xenon flash lamp (lifetime 3.8×10^{-6} sec), and the incident light was passed through a Corning CS 5-60 glass filter. The phosphorescence of 2,3-pentanedione passed through a Corning CS 3-71 filter and was detected by a RCA 1P28 photomultiplier. The output of the photomultiplier was displayed on an oscilloscope and photographed. The quenching abilities of acrolein, crotonaldehyde, and methyl vinyl ketone were determined at the different temperatures by measuring the changes in the pentanedione triplet lifetime when various concentrations of the quenching compounds were present.

The behavior of the triplet state of 2,3-pentanedione in the photolysis of pure pentanedione is described[8] by

$$\mathrm{P} + h\nu \longrightarrow {}^{1}\mathrm{P_v} \longrightarrow {}^{3}\mathrm{P_0}$$

$${}^{3}\mathrm{P_0} \longrightarrow \mathrm{P} + h\nu_\mathrm{p} \qquad k_2 = 47\ \mathrm{sec}^{-1}$$

$${}^{3}\mathrm{P_0} \longrightarrow {}^{3}\mathrm{P_n} \qquad k_3 = 1.3 \times 10^{3}\ \mathrm{sec}^{-1}$$

$${}^{3}\mathrm{P_0} \longrightarrow \text{product?} \qquad k_4 = 10^{11}e^{-11.0/RT}\ M^{-1}\ \mathrm{sec}^{-1}$$

$${}^{3}\mathrm{P_0} + \mathrm{P} \longrightarrow \text{removal} \qquad k_5 = 9 \times 10^{10}e^{-7.5/RT}\ M^{-1}\ \mathrm{sec}^{-1}$$

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