$- E_{A_1}$ with scan rate (see R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969, p 137). These features contrast markedly with the behavior of biscyclooctatetraene.[2]

(9) Molecular orbital calculations on planar **3** using the Hückel approximation predict its energy levels to be $\alpha + 2.39\beta$, $\alpha + 2.00\beta$, $\alpha + 1.70$, $\alpha + 1.59\beta$, $\alpha + 1.41\beta$ (doubly degenerate), $\alpha + 0.86\beta$, $\alpha + 0.36\beta$, and α (doubly degenerate). Consequently, the first two additional electrons enter a nonbonding level.

(10) Extensive effort was made to extract proton–proton coupling constants from the 90- and 300-MHz spectra of this dianion using the INTRCAL program.[12] However, there proved to be too few resolved lines to allow obtention of an acceptable computer-generated least-squares fit.

(11) All assignments have been made with consideration of the earlier work of (a) G. W. Buchanan and A. R. McCarville, *Can. J. Chem.*, **51,** 177 (1973), and (b) H. Günther, A. Shyoukh, D. Cremer, and K. H. Frisch, *Tetrahedron Lett.*, 781 (1974). (c) A. G. Anastassiou and E. Reichmanis, *Angew. Chem., Int. Ed. Engl.*, **13,** 404 (1974).

(12) The benzo portion of the spectrum of **6** has previously been analyzed.[11b] The chemical shifts and coupling constants of the olefinic protons in **6** were herein determined by computer fitting the 300-MHz spectrum with the Nicolet ITRCAL program (which implements the LAOCN3 algorithm on a minicomputer): δ 6.677 (H_c, $H_{c'}$), 6.300 (H_b, $H_{b'}$), and 5.929 (H_a, $H_{a'}$) ($J_{b,c} = J_{b',c'} = 11.89$ Hz, $J_{a,c} = J_{a',c'} = 0.11$ Hz, $J_{a',c} = J_{a,c'} = 0.19$ Hz, $J_{b',c} = J_{b,c'} = 0.07$ Hz, $J_{c,c'} = 0.02$ Hz, $J_{a,b} = J_{a',b'} = 10.89$ Hz, $J_{a',b} = J_{a,b'} = 0.80$ Hz, $J_{b,b'} = 0.24$ Hz, $J_{a,a'} = 9.63$ Hz).

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(14) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41,** 966 (1963).

(15) The Hückel program by J. R. Howles and R. D. Gilliom (QCPE 70) as revised by B. R. Gilson and J. E. Bloor for the IBM 1620 computer was employed.

(16) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972; P. Lazzeretti and F. Taddei, *Org. Magn. Res.*, **3,** 283 (1971); G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97,** 3419 (1975); G. A. Olah, J. S. Staral, and L. A. Paquette, *ibid.*, **98,** 1267 (1976).

(17) This value of $\Delta G^{\ddagger}$ was calculated through use of the equations $1/\tau = \pi^2(\nu_B - \nu_A)^2 [(1/T_2)\text{ exch} - (1/T_2)^0]^{-1}$ and $T_2 = 1/\pi\nu_{1/2}$ (L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Elmsford, N.Y., 1969, p 57). The experimentally determined widths at half-height were $\nu_{1/2}$ (300 K) = 8.3 Hz and $\nu_{1/2}$ (173 K) = 25 Hz.

(18) J. B. Stothers, "Carbon 13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 91.

(19) In the present study, we have also examined the ^{13}C–H coupling constants in the benzotropylium cation (δ 162.2 (J = 163 Hz), 159.8 (167), 145.9 (q), 142.3 (166), 139.9 (169), and 138.9 (171)) and the benzotropenide anion (δ 161.9 (q), 151.2 (139), 126.8 (158), 121.4 (154), 108.0 (153), and 90.7 (155)). The smaller values in the anion are clearly evident, but the full complement of causative effects remain to be addressed.

(20) Addition of hexamethylphosphoramide or 18-crown-6 for solubilization purposes promoted the decomposition of **4.**

(21) This protonation reaction did not afford $C_{18}H_{18}$ cleanly, but also gave di- and octahydro compounds. Such complications could arise as a consequence of the presence of residual Na–K alloy in the mixture and/or because of disproportionation.

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On the Mechanism of Olefin Metathesis

Sir:

Cyclopropanes are converted into metathesis-related olefins over metathesis catalysts[1] in reactions apparently proceeding through interconverting metallocyclobutanes and metal carbenes.[1a] Certain metal–carbene complexes also react with a variety of olefins yielding cyclopropanes and metathesis-related olefins, and metallocyclobutanes have been suggested as the key intermediates.[2] This body of chemistry would seem to interrelate metal–carbene complexes, metallocyclobutanes, and cyclopropanes with olefin metathesis. Indeed, since the initial reports by Casey,[2] demonstrating that tungsten–carbene complexes would react with olefins yielding metathesis-related olefins and cyclopropanes, a general consensus has emerged embracing metal carbenes and metallocyclobutanes as the key, chain-carrying intermediates in olefin metathesis,[1,2-4,] a mechanism proposed earlier by Chauvin.[5]

There remains, however, a number of results which are not easily explained by the Chauvin mechanism. Gassman, for example, has reported the catalytic conversion of a nonconjugated bicyclodiene into a cyclobutane of lower free energy.[6] It proceeds over a metathesis catalyst with remarkable ease.[7] The Chauvin mechanism cannot explain the conversion of olefins into their respective cyclobutanes. It is, therefore, necessary to invoke other reaction paths to explain the transformation of this unusual diolefin by a well-known metathesis catalyst.

Grubbs has shown that his proposed tungstenocyclopentane decomposes at ambient temperatures to metathesized ethylene, the CH_2 groups scrambled to ~12%.[11] The Chauvin mechanism would require the metallocyclopentane to first transform into a metallocyclobutane, a transformation totally without precedent. Assuming that this transformation does not occur, these results would suggest that the observed metathesis proceeded along a path other than that proposed by Chauvin.

I wish to review here some of the recent work supporting the Chauvin mechanism in the context of certain basic principles of thermodynamics.[12] The interrelationship between metal carbenes, metallocyclobutanes, and cyclopropanes which emerges from this work is found to be incompatible with the Chauvin mechanism of olefin metathesis. To illustrate this interrelationship the following hypothetical equilibrium catalytic scheme is constructed:

$$\begin{tikzcd}
& C + X' \arrow[d, shift left] & \\
A + X \arrow[r, shift left] & {[X_1 \rightleftharpoons X_i \cdots X_n]} \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left] & B + X \arrow[l, shift left]
\end{tikzcd}$$

A and B are sets of metathesis-related olefins and C the set of cyclopropanes, products of reductive elimination from the metallocyclobutanes X_i. We shall further assume that this is an equilibrium catalytic reaction, at least in those steps interconverting A and B, in direct accordance with the Chauvin mechanism of olefin metathesis. The extent to which cyclopropanes C would fall into the scheme, interchanging with A and B through the key Chauvin intermediates $[X_1 \rightleftarrows X_i. . .X_n]$ would, of course, depend on the respective free energies of A, B, and C, and the relative rate constants connecting these substrates to the chain-carrying catalytic intermediates. The free energies of the catalytic intermediates paly no role in the scheme since, by definition, a catalyst undergoes no net change (i.e., its net free energy change is zero) in a catalytic transformation.[13]

If the respective free energies of A, B, and C are about equal under metathesis conditions, and we find experimentally that the rate of cyclopropane reaction with the metathesis catalyst is comparable to that of the olefin systems A and B, then microscopic reversibility would demand that the rate of cyclopropane formation be proportionately rapid. Thus, if cyclopropanes are observed to react, generating key, chain-carrying intermediates,[1] then olefin metathesis, an equilibrium catalytic system, should, to some observable extent, yield the respective set of cyclopropanes C, approaching an equilibrium mixture of A, B, and C, if the key catalytic intermediates ($[X_1 \rightleftarrows X_i. . .X_n]$) are those proposed by Chauvin and accepted generally.[3]

At ambient temperatures, the equilibrium constant of the ethylene–cyclopropane system ($3C_2H_4 \rightleftarrows 2C_3H_6$) is ~0.17,[14] corresponding to ~20 mol % cyclopropane at equilibrium. Minor ring substitutions would not be expected to alter the free-energy properties significantly. However, cyclopropanes are not generated over active metathesis catalysts at equilibrium;[8] yet they are reported to react with striking ease.[1a] It is doubtful, however, that the reported reactions proceed along the Chauvin path as suggested. Given the approximately equal free energies of systems A, B, and C, and the necessary consequences of microscopic reversibility, these results would introduce into the scheme the reverse set of reactions, namely the catalytic transformation of A and B into C. It would appear more likely that cyclopropanes indeed react with some tungsten species in the catalyst, possibly generating the metallocyclobutane. The fate of this intermediate, however, would have to compensate for an overall increase in free energy, possibly through the generation of polyalkylidenes, for example cyclopropane → ethylene + polymethylene.

One outstanding example is the reported "vigorous" conversion of cyclopropane to ethylene over a homogeneous metathesis catalyst at −78 °C.[1a] This reaction, however, could not have been a metathesis related catalytic process since the formation of ethylene would be highly unfavored under the conditions (ΔH_f for the conversion of cyclopropane to ethylene is endothermic by 12.02 kcal/mol at 298 K; the equilibrium mole percent cyclopropane at 175 K would then be $\sim$98%).[14] The intermediate tungstenocyclobutane proposed in this reaction is, in my view, a likely one. However, if it reasonably corresponds to the key intermediate in metathesis, it should effect the reverse process with even greater vigor, an observation yet to be reported in ethylene metathesis.[15]

A genuinely catalytic system involving a highly reactive and long-lived homogeneous rhenium catalyst has recently been used in studies of the Chauvin mechanism.[17] In early-quench experiments, preformed metal carbenes reacted with olefins yielding "first-formed" products which proved to contain metathesis-related olefins. However, the "first-formed" products were also rich in cyclopropanes while the products of subsequent olefin metathesis yielded only the usual mix of olefins. It seems most doubtful that the Re catalyst could adopt one kinetic path on its first catalytic turnover yielding cyclopropanes and a different kinetic pathway on subsequent turnovers yielding only olefins. It would appear that the metal carbene was in fact generated and initiated the metathesis. It is also likely that it added to the olefin substrates, generating the respective metallocyclobutanes. These "first-formed" intermediates, however, appear to decompose in accordance with similar species,[2] yielding cyclopropanes and olefins. It is significant that no subsequent intermediate generated throughout the lifetime of the Re catalyst exhibited a similar product selectivity.

Thus, the cyclopropanes of Gassman[1] clearly react with some tungsten species, apparently generating metallocyclobutanes and metathesis-related olefins, and the tungsten carbenes of Casey[2] do add to olefins, very likely generating the metallocyclobutanes which give cyclopropanes[18] and metathesis-related olefins. An important point emerges here, however. Since the collective results constitute direct examples of the two key steps in the above scheme interrelating cyclopropanes (C) and metathesis-related olefins (A and B), *cyclopropanes should, to some observable extent, be products of olefin metathesis given the Chauvin mechanism and the known respective free energies and A, B, and C.*

It has been suggested that cyclopropanes are not products of olefin metathesis because they react completely with the catalyst yielding metathesis-related olefins.[1a] It would seem doubtful that a catalyst would only convert C into A and B, since it would demand that the catalyst alter the equilibrium constant for this system, in direct violation of the first law of thermodynamics. It would seem more likely that the reported body of work only *resembles* the chemistry of metathesis, it does not match it. Metal carbenes (W[2] and Re[17]) clearly add to olefins giving the respective metallocyclobutanes, and cyclopropanes clearly add to a metathesis catalyst generating the metallocyclobutane,[1] but the subsequent chemistry of this key intermediate is consistently in variance with genuine olefin metathesis.[1,2,17,18]

The results of Greenlee and Farona[17] alone, if real, cast serious doubt on the Chauvin mechanism, if not preclude it. To be consistent with the Chauvin mechanism, we must accept that the energy of only one of their metallocyclobutanes, "the first-formed", was favorable for cyclopropane formation and that the energies of all subsequent metallocyclobutanes generated throughout the lifetimes of their "long-lived" catalyst were not. Indeed, all metallocyclobutanes generated in all of the olefin metathesis systems thus far reported must be energetically unique from those examined here[1,2,17,18] in that they obediently partition their kinetic behavior between A and B, never C. The conspicuous absence of cyclopropanes from the voluminous studies reported on olefin metathesis would seem in serious conflict with the reported work offered in support of the Chauvin mechanism.[19]

References and Notes

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(5) J. L. Herisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970).

(6) P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **98**, 861 (1976).

(7) Gassman has shown that ethyl acrylate will quench the metathesis activity for *cis*-2-butene isomerization but will not quench cyclobutane formation.[8] He proposes that the diolefin is reacting along a path distinct from that of other olefins. However, the results could easily reflect preferential coordination of the diolefin. The rate of *cis*-2-butene isomerization, for example, is sharply reduced by 1-nonene.[8] This was a clear example of selective coordination[10] since it was shown that the 1-nonene underwent rapid degenerative metathesis.

(8) P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **98**, 6055 (1976).

(9) M. T. Mocella, M. A. Busch, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1283 (1976).

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(11) R. H. Grubbs and T. K. Brunck, *J. Am. Chem. Soc.*, **94**, 2538 (1972).

(12) For a more detailed discussion of the thermodynamics of catalysis, cf. W. J. Moore, "Physical Chemistry", 3rd ed, Prentice-Hall, Englewood Cliffs, N.J., 1962, p 300.

(13) The structural and free-energy properties of species X and X′ in the scheme have been deliberately left undefined. If they interconvert, a complete catalytic equilibrium obtains. If not, the scheme defines a catalyzed exchange of alkylidene groups between A, B, and C. The overall scheme is only intended to schematically reflect a more complex catalytic system interconnecting separate catalytic cycles, sharing certain key intermediates. Schemes can be drawn in which the catalytic intermediates are interconverted in such a way so as to yield the proper equilibrium stoichiometry (e.g., $2C_3H_6 \rightleftarrows 3C_2H_4$). However, since essentially any equilibrium can, in theory, be catalyzed and therefore appropriate hypothetical schemes drawn, the explicit construction of some arbitrarily chosen scheme would add little to the more generalized model chosen here.

(14) D. R. Stull, E. F. Westrun, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969.

(15) The one case of cyclopropane formation is now believed to be the result of an unrelated side reaction.[16]

(16) J. C. Mol and J. A. Moulijn, *Adv. Catal.*, **24**, 131 (1975).

(17) W. S. Greenlee and M. F. Farona, *Inorg. Chem.*, **15**, 2129 (1976).

(18) The tungsten–carbene complex is only ment to model the chemistry of metathesis. The formation of metathesis-related olefins is the crux of the evidence in support of the Chauvin mechanism. If, however, the model realistically reflects the chemistry of a key intermediate, then the results should also indicate that no significant energy difference separates the transformation of the metallocyclo into the olefin and the cyclopropane.

(19) Various statistical analysis[4] have been offered in support of a chain mechanism for metathesis (i.e., the Chauvin path) over the "pair-wise" metal–cyclobutane path. However, certain difficulties associated with determining "first-formed" products in highly active systems have been noted.[3c] It should also be noted that the results obtained would be consistent with both mechanisms if the catalytic species (both homogeneous and

heterogeneous) are clusters of active sites and that the rates of alkylidene scrambling with a represenative number of olefins coordinated to a given cluster is faster than olefin escape from the cluster. Clustering in homogeneous systems involving highly unsaturated transition metals (e.g., reduced group 4b metal complexes) would not be unusual.

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Aperiodic and Periodic Oscillations in Fluorescence Intensity from Irradiated Chlorocarbon Solutions of Anthracene and 9,10-Dimethylanthracene

Sir:

We wish to report some unusual results concerning the fluorescence of anthracene and 9,10-dimethylanthracene in chlorocarbon solutions. Our observations add to the known examples of photoinduced *chemical instabilities.*[1] The findings are important, in part, because an analytical procedure[2] for determination of certain organic materials in water involves extraction with a chlorocarbon followed by a fluorescence determination in another solvent. This work was initiated by the desire to carry out the fluorescence measurement in the extraction solvent. Under certain conditions, we find that excitation of the fluorescence of anthracene and 9,10-dimethylanthracene also results in photoinduced chemistry giving rise to aperiodic and periodic *oscillations* in emission intensity.

Both anthracene and 9,10-dimethylanthracene are well-characterized substances with respect to luminescence properties,[3] and each fluoresces in the blue with a good quantum efficiency which is independent of the excitation wavelength. We observed these typical properties in aliphatic hydrocarbons like cyclohexane, but in $CHCl_3$ solutions some unusual results were found. Excitation of a quiet $CHCl_3$ solution of $\sim 10^{-5}$ M anthracene or 9,10-dimethylanthracene at 260 nm gives fluorescence which varies in time in a periodic or aperiodic oscillating manner. The observation was first made with an Aminco-Bowman emission spectrophotometer (by R.J.B.) and was subsequently repeated in a second laboratory with a Hitachi-Perkin Elmer MPF3 emission spectrophotometer (M.S.W.).

In both cases, the oscillation in fluorescence intensity was found to occur under the conditions where 298 K fluorescence spectra are normally recorded. In all cases where oscillatory behavior was observed, the sample volume was significantly larger than the irradiated volume. Stoppered, but not degassed, ~3-cc samples in square (1.00 × 1.00 cm i.d.) fluorescence cells were typically used, and the $CHCl_3$ (and the other chlorocarbons) was either spectroquality or reagent grade and used as received. The anthracene and 9,10-dimethylanthracene were obtained from several different suppliers and used as received. The point is that the behavior to be described below is easy to observe and the essential results are independent of the sources

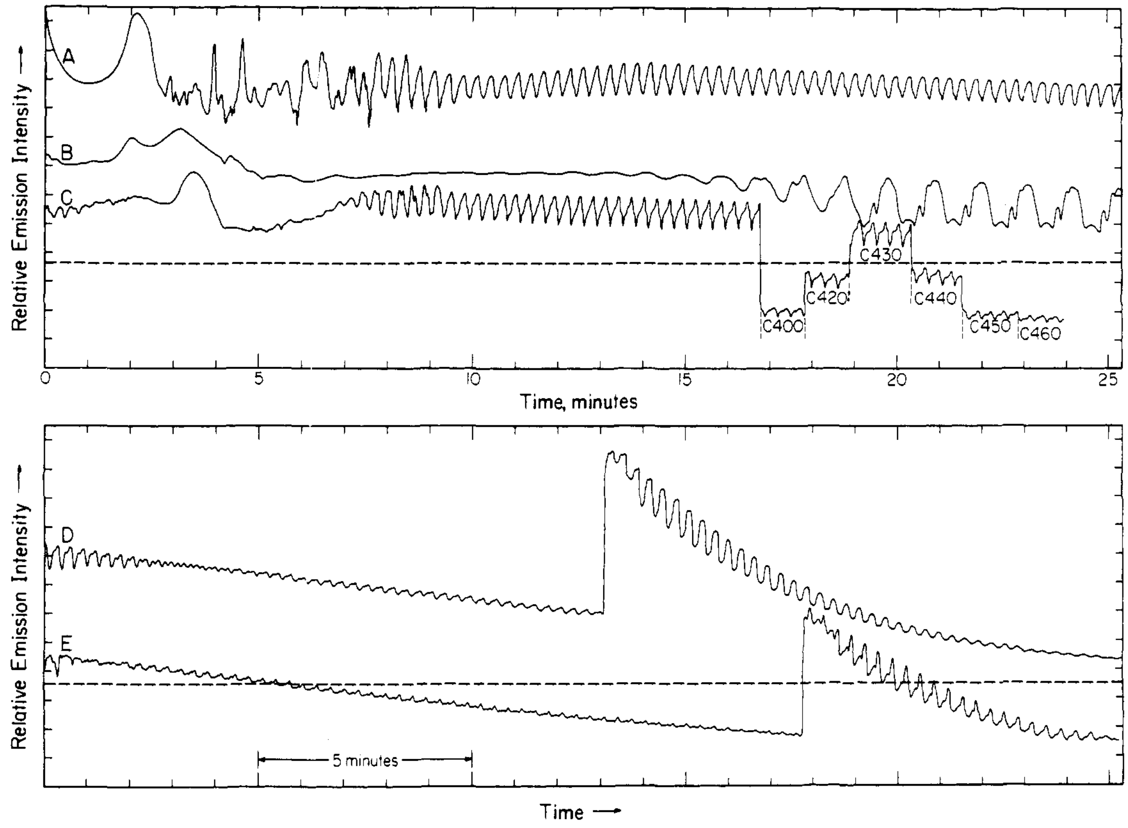

Figure 1. Plots of 9,10-dimethylanthracene (DMA) fluorescence intensity against time in ~3 cc of $CHCl_3$ solution at 298 K. All plots were obtained using a Perkin-Elmer MPF3 emission spectrophotometer and the sample was in a square (1.0 × 1.0 cm i.d.) fluorescence cell. All curves are for an excitation wavelength of 260 nm (slit 16 nm) and a monitoring wavelength of 410 nm (slit 6 nm) unless specified otherwise. Curve A: the baseline is the dashed horizontal line in the upper half of the figure; [DMA] = 2.0×10^{-5} M. Curve B: the baseline is at the solid horizontal line of the upper half of the figure: [DMA] = 4.0×10^{-5} M. Curve C: the baseline is as in curve B, and the sample is just a fresh solution of that used in curve A: the excitation and emission slits are the same, but the monitoring wavelength is 410 nm only up to *T* 16.7 min (during the intervals marked C400, C420, C430, C440, C450, and C460 the monitoring wavelength was 400, 420, 430, 440, 450, and 460 nm, respectively). Curve D: the baseline is the dashed horizontal line of the lower half of the figure; [DMA] = 1.0×10^{-5} M; the ~25-min time interval shown is 15 min after the start of the irradiation (the sharp increase in intensity corresponds to the point where the excitation slit was opened from 16 nm to 40 nm to increase the light intensity by a factor of ~3.3). Curve E: repeat of curve D except the baseline is the solid line at the bottom of the lower half of the figure.