

Figure 1. The  $\text{RhCl}((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{C}_4(\text{CF}_3)_4$  molecule with the phenyl rings omitted for clarity.

structural evidence has been presented. In view of the great interest in this area, we wish to communicate the preliminary results of a structural study on the complex prepared from  $\text{RhCl}(\text{Sb}(\text{C}_6\text{H}_5)_3)_3$  and hexafluorobutene-2 which show that a rhodacyclopentadiene moiety is indeed present as originally postulated.<sup>3</sup>

Chlorobis(triphenylstibine)tetrakis(trifluoromethyl)rhodacyclopentadiene crystallizes as yellow-orange prisms from methylene chloride-diethyl ether. When prepared in this manner the complex is obtained as a dichloromethane solvate. The systematic absences  $h0l$  for  $l = 2n + 1$  and  $0k0$  for  $k = 2n + 1$  observed on Weissenberg and precession photographs ( $\text{Cu K}\alpha$  radiation) uniquely determine the space group as  $\text{P2}_1/\text{c}$  ( $\text{C}_{2h}^2$ , No. 14).<sup>6</sup> The monoclinic unit cell has  $a = 13.257$ ,  $b = 25.592$ ,  $c = 16.801$  Å;  $\beta = 125.58^\circ$ ;  $V = 4636$  Å<sup>3</sup>. The observed density of 1.75 g/cc agrees well with the calculated value of 1.797 g/cc for  $Z = 4$ . A total of 3418 unique reflections within the sphere having  $\sin \theta/\lambda \leq 0.5$  were collected on a Picker, automated, four-circle diffractometer ( $\text{Cu K}\alpha$  radiation, Ni filtered) using the  $\theta$ - $2\theta$  scan procedure. Of these, 158 were considered to be unobserved, and all data were corrected for absorption ( $\mu = 137.2 \text{ cm}^{-1}$ ). The structure was solved by Patterson and difference-Fourier techniques and refined by block-diagonal least-squares methods to a current conventional residual of 0.101 with all nonhydrogen atoms except for the phenyl group carbons allowed to vibrate anisotropically. Refinement is continuing with attempts being made to better treat the large thermal motions of the trifluoromethyl groups (particularly those containing  $\text{C}_6$  and  $\text{C}_7$ ).

Figure 1 gives a perspective view of the molecule. The data clearly show that the fluorocarbon moiety is  $\sigma$ -bonded to the rhodium giving a rhodacyclopentadiene ring which is planar within experimental error ( $\sigma_{\text{ring}} = 0.02$  Å). Relevant angles are  $\text{Sb}_2\text{-Rh-Cl}_1$ ,  $88^\circ$ ;  $\text{Sb}_1\text{-Rh-Cl}_1$ ,  $90^\circ$ ;  $\text{Sb}_1\text{-Rh-Sb}_2$ ,  $178^\circ$ ;  $\text{Cl}_1\text{-Rh-C}_1$ ,  $139^\circ$ ;  $\text{Cl}_1\text{-Rh-C}_4$ ,  $142^\circ$ ;  $\text{C}_1\text{-Rh-C}_4$ ,  $78^\circ$ ;  $\text{Rh-C}_1\text{-C}_2$ ,  $118^\circ$ ;  $\text{C}_1\text{-C}_2\text{-C}_3$ ,  $113^\circ$ ;  $\text{C}_2\text{-C}_3\text{-C}_4$ ,  $115^\circ$ ;  $\text{C}_3\text{-C}_4\text{-Rh}$ ,  $117^\circ$ . The coordination about rhodium is thus that of a slightly distorted trigonal bipyramid. The data further indicate that the solvent molecule has no strong tendency to oc-

cupy a sixth coordination position about rhodium since the angles  $\text{Cl}_1\text{-Rh-C}_1$  and  $\text{Cl}_1\text{-Rh-C}_4$  are very nearly equal.

It can be seen from Figure 1 that although the distances  $\text{C}_1\text{-C}_2$  and  $\text{C}_3\text{-C}_4$  are not significantly different from the corresponding values for 1,3-butadiene (1.337 (5) Å), the  $\text{C}_2\text{-C}_3$  distance is noticeably shorter ( $\Delta/\sigma \sim 3$ ) than in the latter compound ( $\text{C}_2\text{-C}_3 = 1.483$  (10) Å in  $\text{C}_4\text{H}_6$ ).<sup>7</sup> Also, the  $\text{Rh-C}_1$  and  $\text{Rh-C}_4$  distances appear shorter than that found in  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{IC}_2\text{F}_5$  (2.08 (3) Å),<sup>8</sup> but when account is taken of the difference in radius between  $\text{sp}^2$  and  $\text{sp}^3$  carbon atoms ( $\sim 0.03$  Å) this difference is not significant at the level of accuracy of our determination. If the metal is considered to be formally  $\text{Rh(III)}$ , it lacks two electrons of possessing the rare gas configuration when  $\pi$  interaction with the rest of the ring is neglected. It would appear that although some degree of delocalization in the ring is likely, it is not possible at this point to draw any definite conclusions concerning it, and in particular no assessment can yet be made to what extent there is  $\text{Rh-C}$  multiple bonding. The fact that the complex reacts readily with donors such as carbon monoxide suggests that the tendency of the metal to attain the rare gas configuration through  $\pi$  overlap with the remainder of the ring is probably not very large. Hopefully more definite conclusions concerning this point can be reached when the structure is further refined.

**Acknowledgment.** We thank Dr. Charles Fritchie, Jr., for the use of the diffractometer.

(7) Special Publication No. 18, The Chemical Society, London, 1965, M109s.

(8) M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).

Joel T. Magee

Department of Chemistry, Tulane University  
New Orleans, Louisiana 70118

Received April 7, 1969

## The Thermal Dependence of Photoannulation<sup>1</sup>

Sir:

The effects of temperature on photochemical reactions in the condensed phase have been but sporadically studied. The references to a thermal effect in photoannulation are even more sparse although in a few specific cases the products and quantum efficiency have been shown to be temperature dependent.<sup>2</sup> We wish to report here the results of our study of temperature variation on the photoaddition of 2-cyclopentenone to olefins. The observations are striking and suggest immediate practical consequences. They may be interpreted, also, as supporting our present hypothesis of reversible intermediate formation in photoannulation.

In Table I are given the quantum yields of adduct formation from 2-cyclopentenone and four olefins at several different temperatures.<sup>3</sup> It can be seen that the quantum efficiencies do depend on temperature, and to different extents with different olefins. With *trans*-3-

(1) Photochemical Synthesis, Part XXVII. Part XXVI: P. de Mayo, A. A. Nicholson, and M. F. Tchir, *Can. J. Chem.*, **47**, 711 (1969).

(2) See, for instance, A. Cox, P. de Mayo, and R. W. Yip, *J. Amer. Chem. Soc.*, **88**, 1043 (1966); D. Bryce-Smith and A. Gilbert, *Chem. Commun.*, 19 (1968).

(3) Details of the apparatus and procedures used will be published at a later date. All irradiations, including Stern-Volmer plots, were performed on an optical bench.

(6) "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1959.

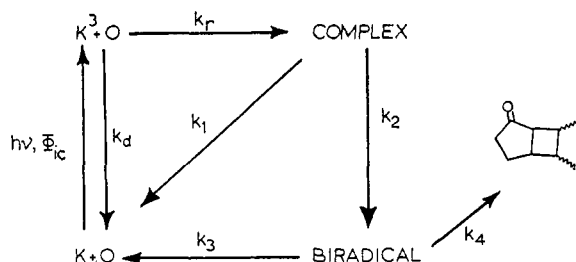


Figure 1. A possible scheme: K = cyclopentenone, O = olefin.

hexene decreasing the temperature slightly decreases the quantum yield, while with cyclopentene the quantum yield is more than doubled over the same temperature range.

Table I. Temperature Dependence of Quantum Yields

Olefin	$\Phi_{27^\circ}$	$\Phi_{-10^\circ}$	$\Phi_{-71^\circ}$
Cyclohexenes <sup>a</sup>	0.46	0.51	0.62
Cyclopentene	0.23	0.31	0.61
cis-Dichloroethylene	0.23		0.34
trans-3-Hexene	0.22		0.19

<sup>a</sup> Other quantum yields: 0.55 at  $-41^\circ$ ; 0.68 at  $-90^\circ$ ; 0.72 at  $-102^\circ$ .

It has recently been suggested that the reaction of cyclopentenone with olefins<sup>4</sup> and with itself<sup>5</sup> proceeds via a discrete intermediate (or intermediates) which can partition between formation of the observed products and reversion to ground-state ketone and olefin. The nature of the intermediate(s) is not presently known but two possibilities exist: a complex (possibly charge transfer) and/or a 1,4 biradical. A simple mechanism, which includes both intermediates in sequence, is given in Figure 1.

Taking into account the existence of this intermediate and with the usual steady-state assumptions, it is possible to derive the expression

$$\Phi = \Phi_{ic} K \left( \frac{k_r [\text{olefin}]}{k_r [\text{olefin}] + k_d} \right) \quad (1)$$

for the quantum yield of product formation, where  $\Phi_{ic}$  is the intersystem crossing efficiency,  $k_r$  is the rate constant for (first) intermediate formation,  $k_d$  is the unimolecular decay constant, and  $K$  is the fraction of the intermediate that gives product and is given by the expression

$$K = \left( \frac{k_4}{k_3 + k_4} \right) \left( \frac{k_2}{k_1 + k_2} \right) \quad (2)$$

The observed change in quantum efficiency might be due to one of several causes: increased yield of the reactive triplet, increased  $k_r$ , decreased  $k_d$ , or an increase in the value of  $K$ . The first possibility can be dismissed since it has been shown that the quantum yield of intersystem crossing is near unity at room temperature.<sup>6</sup> To determine if the effect were due to a change in either  $k_r$  or  $k_d$  the two rate constants were determined at two temperatures, using cyclohexene as the substrate. Dilution (inversion of eq 1) gives the

(4) Part XXVI (see ref 1).

(5) P. J. Wagner and D. J. Bucheck, *Can. J. Chem.*, **47**, 713 (1969).

(6) P. de Mayo, J.-P. Pete, and M. F. Tchir, *ibid.*, **46**, 2535 (1968).

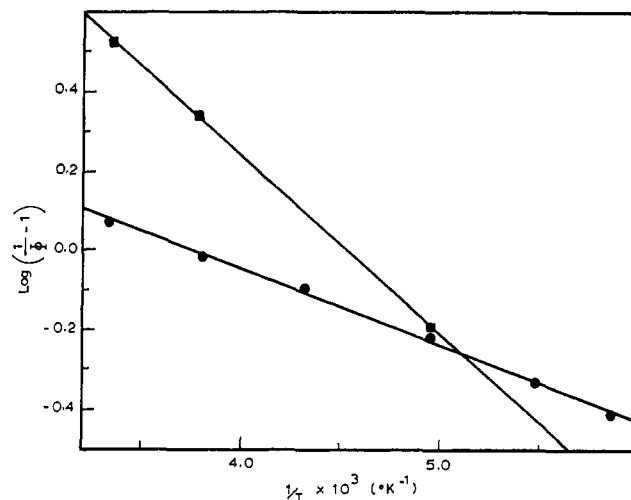


Figure 2. Arrhenius plot: ●, cyclohexene; ■, cyclopentene.

ratio of  $k_d/k_r$  while quenching (Stern-Volmer plot) yields the sum of the two rates. The determined change in  $k_r$  is seen to be approximately proportional to the change in the diffusion rate (Table II), i.e., it

Table II. Temperature Dependence of Rate Constants

Temp, $^\circ\text{C}$	$k_{diff} \times 10^{-1}, \text{ } M^{-1} \text{ sec}^{-1}$	$k_d \times 10^{-8}, \text{ sec}^{-1}$	$k_r \times 10^{-8}, \text{ } M^{-1} \text{ sec}^{-1}$
20	2.0	1.5	10.3
-71	0.36	1.3	3.2

<sup>a</sup> Calculated from the Debye equation using measured viscosities.

<sup>b</sup> Other values for  $k_d$  (at  $20^\circ$ ) range from  $8 \times 10^7$  to  $1.7 \times 10^8 \text{ sec}^{-1}$ .<sup>4,5</sup> Whether the variation is real or is merely a result of the experimental procedure used is not known at this time.

decreases with temperature. The change in  $k_d$  with temperature, a slight decrease, is similar to that reported by Zimmerman for a cyclohexenone derivative.<sup>7</sup> However, it is evident that the last bracketed term in eq 1 is, at the concentration of olefin used, near 0.9 at both temperatures, and a change in  $k_d$  cannot produce a large change in  $\Phi$ . The conclusion follows that the large changes in quantum yields, at least, result from changes in the partition function,  $K$ .

Since the nature and number of the intermediate(s) is not known, it is impossible to assign values to the rate constants which go into making  $K$ . Two possible extremes, however, can be treated:  $k_2 \gg k_1$  or  $k_4 \gg k_3$ . If the bracketed term in eq 1 is assumed to be temperature independent (see above) and has a value of unity, for the sake of simplicity, then an Arrhenius-type expression can be derived

$$\log \left( \frac{1}{\Phi} - 1 \right) = \log A + \frac{\Delta E_a}{2.303RT} \quad (3)$$

where  $A$  is a ratio of preexponential factors and  $\Delta E_a$  is a difference in activation energies.

In Figure 2 are shown the plots of eq 3 for cyclohexene and cyclopentene. Whatever the validity of the assumptions may be, the plots do approximate straight lines. The difference between the activation energies for the competing processes in the two olefins are

(7) H. E. Zimmerman and W. R. Elser, *J. Amer. Chem. Soc.*, **91**, 887 (1969).

−0.9 kcal/mol (cyclohexene) and −2.1 kcal/mol (cyclopentene).

From the synthetic point of view the present observations have two consequences. Firstly, there is noted here the minor effect previously observed in the addition of maleic ester to cyclohexene,<sup>2</sup> that a change in temperature may lead to a change in isomer composition in a particular photoannulation. Secondly, as reported here for the case of cyclopentene and cyclohexene, the preference for an addition to one of two substrates may be modified with a change in temperature. This may lead, in future studies to possible selectivity in addition to polyfunctional substrates.

(8) Holder of a National Research Council Studentship, 1966–present.

R. O. Loutfy, P. de Mayo, M. F. Tchir<sup>8</sup>

Department of Chemistry, University of Western Ontario  
London, Ontario, Canada

Received April 19, 1969

### Application of Ion Cyclotron Resonance to the Structure Elucidation of the $C_3H_6O^+$ Ion Formed in the Double McLafferty Rearrangement<sup>1,2</sup>

Sir:

The mass spectrum of a dialkyl ketone containing one or more  $\gamma$ -hydrogen atoms in each alkyl group usually exhibits an intense peak corresponding to the consecutive rearrangement of two  $\gamma$ -hydrogen atoms accompanied by  $\beta$  cleavage, a process generally known as the "double McLafferty rearrangement."<sup>3</sup> The second step of the decomposition can be envisaged as occurring in two ways: hydrogen transfer could proceed either to the enolic oxygen ( $b \rightarrow c$ ), or to the enolic double bond ( $b \rightarrow d$ ).<sup>4</sup> A number of methods have been utilized in an effort to determine the structure of the double McLafferty ion. On the basis of metastable ion characteristics,<sup>6</sup> McLafferty and Pike have concluded that "a substantial part of the  $C_3H_6O^+$  ions from 4- and 5-alkanones must not correspond to" structure d.<sup>6a</sup> Furthermore, MO calculations have been presented which suggest that the transition state for transfer to the enolic oxygen is of lower energy than the transition state for the alternative process.<sup>7</sup> On the other hand, ion cyclotron resonance (icr) experiments<sup>5</sup> have tended to support the alternative structure d.

(1) Paper CLXXVII in the series "Mass Spectrometry in Structural and Stereochemical Problems." For preceding paper see L. Tökés and C. Djerassi, *J. Am. Chem. Soc.*, in press.

(2) Financial assistance by the National Institutes of Health (Grants AM-12758 and AM-04257) is gratefully acknowledged. We are indebted to Professor J. D. Baldeschwieler for generously providing access to his ion cyclotron resonance spectrometer, which was purchased on funds supplied by the National Science Foundation (GP 4924-X), NASA (NGL 05-020-S1), and the Center for Materials Research, Stanford University.

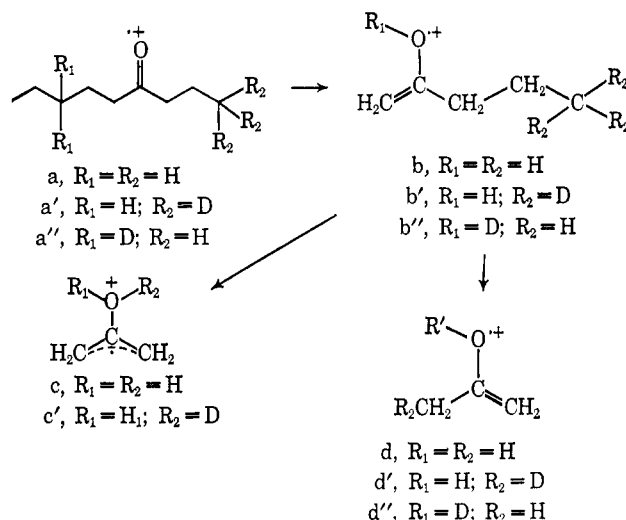
(3) For a summary see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1967, pp 155–162.

(4) Mechanisms requiring ketonization of the intermediate enol ion b are unlikely in light of recent evidence that ketonization does not occur under ordinary electron impact (J. K. MacLeod, J. B. Thomson, and C. Djerassi, *Tetrahedron*, **23**, 2095 (1967)) or icr<sup>5</sup> experimental conditions.

(5) J. Diekmann, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **91**, 2069 (1969).

(6) (a) F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967); (b) F. W. McLafferty, T. Wachs, and W. T. Pike, *Advan. Mass. Spectrom.*, **4**, 153 (1968); (c) W. F. Haddon and F. W. McLafferty, *J. Am. Chem. Soc.*, **90**, 4745 (1968).

(7) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Am. Chem. Soc.*, **90**, 7239 (1968).



The theory, instrumentation, and applications of icr spectroscopy have already been described in considerable detail.<sup>8</sup> Icr single-resonance spectra are similar to ordinary mass spectra, except that ion–molecule reactions are readily observed. Consider the reaction  $AH^+ + B \rightarrow A + BH^+$ . By using pulsed double-resonance and phase-sensitive detection, the signal from  $BH^+$  can be monitored while an irradiating radiofrequency field is swept through a range of frequencies. When the irradiating frequency equals the natural cyclotron frequency of  $AH^+$ , the translational energy of  $AH^+$  increases. Because reaction rate constants are generally energy dependent, the population of  $BH^+$  changes, and this change produces a peak in the double-resonance spectrum. Thus, if the irradiating frequency is swept through the cyclotron frequencies of all ions, it is possible to determine the genesis of the product ion.

In a previous paper,<sup>7</sup> seven ion–molecule reactions capable of distinguishing between the keto and enol forms of the McLafferty ion were described; in every case, the double McLafferty ion and the independently generated enol ion (d) reacted identically. Since there is no precedent for ions of different structure exhibiting identical reactivity, it was concluded tentatively that the correct structure is d rather than c. Therefore, further investigation of the double McLafferty ion was undertaken, and icr was again the technique chosen for use.

It has been established that secondary hydrogens participate in the single McLafferty rearrangement ten to twenty times as readily as primary ones.<sup>9</sup> It has also been demonstrated that only hydrogens directly bonded to oxygen are transferred from the single and double McLafferty ions to neutral ketones.<sup>7</sup> Thus, the possibility of generating and detecting a specifically labeled double McLafferty ion exists. For example, 4-nona-1,1,1- $d_3$  (I) could produce either c' or d'. The latter has only protium bonded to oxygen, and thus can donate only protium to neutral 4-nonanone. On the other hand, ion c' has both protium and deuterium bonded to oxygen and would be expected to transfer both to 4-nonanone. Observation of the mass 147 ( $M + 2$ ) ion with irradiation through the appropriate mass range (Figure 1a) indicates almost no contribution

(8) (a) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); (b) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1967.

(9) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966).