be summarized as follows: (a) Molecular ions of ketones are very unstable toward dissociation. Even a slight enhancement of their kinetic energy is sufficient to induce dissociation upon collisions. (b) For ketones having at least one alkyl group larger than methyl thermal collisions induce an isomerization of the molecular ion. It seems rather attractive to describe this reaction as a keto-enol isomerization but at present our experiments do not allow this onclusion. The reverse reaction has previously been observed for activated enol ions obtained by a McLafferty rearrangement.[13,14] (c) Solvated fragment ions are formed both by the well-known self-acylation of the molecular ion and by direct clustering of fragments with neutral molecules. This leads to pressure-dependent double-resonance signals.

The reaction scheme proposed by Tiedemann and Riveros is clearly incomplete. One might even ask whether the formation of dimer ions according to scheme 3 is really true. Since the molecular ions of ketones, other than acetone, both isomerize and give rise to dimer ions, it might be possible that the dimer ion is in fact an enol ion complexed with a keto molecule.

**Acknowledgment.** Research on ion-molecule reactions with ICR in the Department of Theoretical Organic Chemistry at the University of Leiden was initiated by the late Professor L. J. Oosterhoff. We thank the Netherlands Organization for the Advancement of Pure Research (SON/ZWO) for financial support.

## References and Notes

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

(2) M. M. Bursey, J. Kao, J. D. Henion, C. E. Parker, and T. S. Huang, *Anal. Chem.*, **46**, 1709 (1974).

(3) D. A. Chatfield and M. M. Bursey, *J. Am. Chem. Soc.*, **97**, 3600 (1975).

(4) D. A. Chatfield and M. M. Bursey, *J. Chem. Soc., Faraday Trans. 1*, **72**, 417 (1976).

(5) K. A. G. MacNeil and J. H. Futrell, *J. Phys. Chem.*, **76**, 409 (1972).

(6) P. W. Tiedemann and J. M. Riveros, *J. Am. Chem. Soc.*, **95**, 3140 (1973).

(7) P. C. Isolani, J. M. Riveros, and P. W. Tiedemann, *J. Chem. Soc., Faraday Trans. 2*, **69**, 1023 (1973).

(8) A. Maquestiau and J. van Thuijl, private communication.

(9) T. B. MacMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).

(10) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.

(11) F. Kaplan, *J. Am. Chem. Soc.*, **90**, 4483 (1968).

(12) In principle one should be able to observe the change in reactivity from the curve for the molecular ion itself. Our attempts to do so were not successful because at least with our ICR cell ion losses during the transport of ions to the analyzer section by the drift pulse seem to be largest at short trapping times. This results in a distortion of the curves for primary ions at the short trapping times where the isomerization is to be observed.

(13) D. J. McAdoo, F. W. Lafferty, and T. W. Parks, *J. Am. Chem. Soc.*, **94**, 1601 (1972).

(14) J. R. Hass, M. M. Bursey, D. G. I. Kingston, and H. P. Tannenbaum, *J. Am. Chem. Soc.*, **94**, 5095 (1972).

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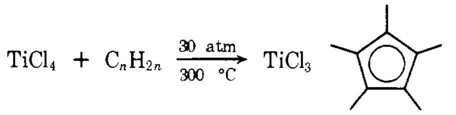
# Ion-Molecule Reactions in Mixtures of $TiCl_4$ with Olefins in the Gas Phase

**John Allison and D. P. Ridge***

*Contribution from the Department of Chemistry, University of Delaware, Newark, Delaware 19711.* *Received June 21, 1976*

**Abstract:** Reactions between small olefins and species formed by electron impact on $TiCl_4$ are described. Rate constants determined by an ion cyclotron resonance technique are reported. $Ti^+$ and $TiCl^+$ complex with the olefins and eliminate hydrogen. $TiCl_2^+$ and $TiCl_3^+$ complex with the olefins and eliminate HCl. In addition, $TiCl^+$, $TiCl_2^+$, and $TiCl_3^+$ also complex with olefins containing a chain of five or more carbons and eliminate smaller olefins. $TiCl_4^+$ is unreactive. General patterns of reactivity and possible reaction mechanisms are discussed.

In solution titanium tetrachloride participates in a variety of interesting reactions with alkenes. In the Ziegler-Natta scheme[1,2] for polymerization of olefins, $TiCl_4$ in combination with aluminum alkyls performs a catalytic function. The process is postulated to occur through ionic- and ion-pair intermediates.[1] Roehl, Lange, Golsal, and Roth[3] report that $TiCl_4$ itself reacts with almost any alkene according to reaction 1.



+ by-products (1)
($H_2$, HCl, alkenes, alkanes)

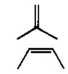
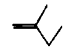
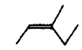
The gas phase ion chemistry of $TiCl_4$ with olefins includes a number of processes which may be elementary steps in the solution chemistry of $TiCl_4$ with olefins. Ions formed by electron impact on $TiCl_4$ form complexes with olefins. The complexes lose $H_2$, HCl, and smaller olefins. Properties of the products of these dissociative additions may be deduced from their further reactions. The overall reaction schemes are quite specifically related to the structure of the olefins. Following an account of experimental procedures, we give below the reaction schemes in detail and discuss the relationship between olefin structure and reactivity.

## Experimental Section

All experiments were performed on an ion cyclotron resonance[4] instrument of conventional design described elsewhere.[5] Reaction pathways were identified by observing reactant and product ion signal intensities as a function of pressure and by double resonance. Rate constants were determined from single resonance spectra by the method of Comisarow.[6] Reported rate constants represent the average of at least three determinations. The uncertainty in the reported rate constants arises from uncertainty in pressure measurements made with an MKS Baratron Capacitance Manometer and the noise level in the single resonance spectra. Except as noted below, the estimated errors are $\pm 20\%$ or $\pm 0.2 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, whichever is greater.

$TiCl_4$ was obtained from Alfa Products. Impurities were minimized by multiple freeze-pump-thaw cycles using an acetonitrile-$CO_2$ bath.

Table I. Rate Constants[a] for Reactions of $Ti^+$ with Olefins[b]

| Olefin | Neutral products: $2H_2$ | $H_2$ | $k_L$[c] |
|---|---|---|---|
|  | | 6.2 | 13.0 |
|  | | 2.7 | 13.0 |
|  | | | 14.0 |
|  | | | 14.0 |
|  | 10.5 | | 15.0 |
|  | 7.0 | | 15.0 |
|  | 3.6 | | 14.0 |
|  | | | 15.0 |
|  | | | 15.4 |

[a] Numbers tabulated are $k \times 10^{10}$ in $cm^3$ $molecule^{-1}$ $s^{-1}$. Reactions with rates $<1 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ would not be observed. Uncertainty in the rate constants is ±20% or $\pm 1 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, whichever is greater. [b] All reactions are bimolecular dissociative additions involving elimination of the indicated molecules.

Commercial samples of hydrocarbons were used as supplied except for freeze–pump–thaw cycles. The mass spectra of the hydrocarbons confirmed their purity.

In a typical experiment, $TiCl_4$ was admitted to a pressure of approximately $10^{-6}$ Torr. Through a second inlet the alkene was admitted initially in an equal amount. Spectra were taken after subsequent additions of the alkene to a pressure where the $TiCl_4$:$C_nH_{2n}$ ratio was approximately 1:10.

## Results

The 70 eV mass spectrum of $TiCl_4$ at a pressure of $1 \times 10^{-6}$ Torr consists of $Ti^+$ (3.4%), $TiCl^+$ (6.2%), $TiCl_2^+$ (11.5%), $TiCl_3^+$ (45.7%), $TiCl_4^+$ (33.2%).[7] The reactions of each of these species with a series of olefins are summarized in Tables I–IV. The general reaction scheme observed is:

$$\begin{tikzcd}
TiCl_nC_mH_{2m-2}{}^+ \arrow[r, "-H_2"] & TiCl_nC_mH_{2m-4}{}^+ \arrow[r, "-H_2"] & TiCl_nC_mH_{2m-6}{}^+ \\
TiCl_n + C_mH_{2m} \arrow[u, "-H_2"] \arrow[r, "-HCl"] \arrow[d, "-C_rH_{2r}"] & TiCl_{n-1}C_mH_{2m-1}{}^+ & \\
TiCl_nC_{m-r}H_{2m-2r}{}^+ & &
\end{tikzcd}$$

$Ti^+$ participates in $H_2$ elimination reactions. $H_2$ elimination from hydrocarbons has been reported by Müller on a $Ni^+$ metal center.[8] Since $Ti^+$ is of small abundance in the $TiCl_4$ mass spectrum, reactions with rate constants less than approximately $1 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ could not be observed, as indicated in Table I. When the reactant alkene contains a five-carbon chain or longer, loss of two molecules of hydrogen occurs. No HCl or alkene eliminations were observed with this reactant ion.

$H_2$ elimination also dominates the reactions of $TiCl^+$ as summarized in Table II. If the alkene contains a four-carbon chain or smaller, only one molecule of $H_2$ is eliminated. If the alkene contains a five-carbon chain on longer, two and three molecules of $H_2$ are eliminated. $TiCl^+$ also participates in two reactions involving cleavage of carbon–carbon bonds: 2-heptene reacts to lose propene and $H_2$ (or propane) forming $TiClC_4H_6^+$, and 1-pentene reacts to lose ethylene forming $TiClC_3H_6^+$.

With two halogens bound to the metal, $TiCl_2^+$ reacts with the smaller branched olefins to eliminate HCl (Table III). In the methylpentenes, both $H_2$ and HCl are lost. The straight chain alkenes react with $TiCl_2^+$ to eliminate smaller alkenes. 1-Pentene loses ethylene, and 1-hexene and 2-heptene lose $C_3H_6$.

Similarly, as indicated in Table IV, $TiCl_3^+$ reacts with the butenes and substituted pentenes to eliminate HCl. It reacts with 1-heptene via ethylene elimination, with 1-hexene primarily via butene elimination, and with 2-heptene via butene and pentene elimination.

$TiCl_4^+$ is unreactive with the alkenes.

Subsequent reactions of several of the metal alkene complexes were observed.

$$TiC_6H_8^+ + C_6H_{12} \rightarrow TiC_{12}H_{19}^+ + H \qquad (2)$$

Reaction 2 was observed in both methylpentene-$TiCl_4$ mixtures with $k = 6.9 \pm 1.4 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ for *cis*-3-methyl-2-pentene and $k = 7.4 \pm 1.5 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ for 2-methyl-2-pentene. Substitution reactions 3 and 4 were

$$TiCl_3C_2H_4^+ + 1\text{-}C_6H_{12} \rightarrow TiCl_3C_6H_{12}^+ + C_2H_4 \qquad (3)$$

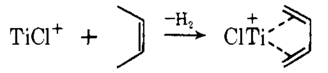
$$TiCl_2C_3H_6^+ + 1\text{-}C_6H_{12} \rightarrow TiCl_2C_6H_{12}^+ + C_3H_6 \qquad (4)$$

observed in the 1-hexene-$TiCl_4$ mixture reactions with rate constants of $7.4 \pm 1.5 \times 10^{-10}$ and $5.5 \pm 1.1 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, respectively. Analogous reactions are observed for $TiCl_3C_2H_4^+$ ($k = 1.8 \pm 0.4 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) and $TiCl_3C_3H_6^+$ ($k = 1.0 \pm 0.2 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) with 2-heptene and for $TiCl_3C_2H_4^+$ with pentene ($k = 1.1 \pm 0.2 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$).

## Discussion

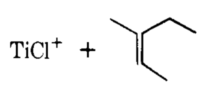
The general features of the dissociative addition reactions of $TiCl_n^+$ with olefins are: (1) $Ti^+$ and $TiCl^+$ eliminate one molecule of hydrogen from butenes. (2) $Ti^+$ and $TiCl^+$ eliminate two or three molecules of hydrogen from pentenes and larger olefins. (3) $TiCl_2^+$ and $TiCl_3^+$ eliminate HCl from butenes and methylpentenes. (4) $TiCl^+$, $TiCl_2^+$, and $TiCl_3^+$ eliminate smaller olefins from unbranched alkenes.

**$Ti^+$ and $TiCl^+$ Reactions.** The $Ti^+$ and $TiCl^+$ ions have four and three vacancies, respectively, in their normal coordination shells. This may be the reason for the predominance of $H_2$ elimination in the chemistry of these ions. Elimination of $H_2$ from substrate olefins may help fill the vacancies as suggested in reaction 5. Structures similar to that of the product of reaction 5 seem probable for the products of reaction of $Ti^+$ and $TiCl^+$ with the methylbutenes.

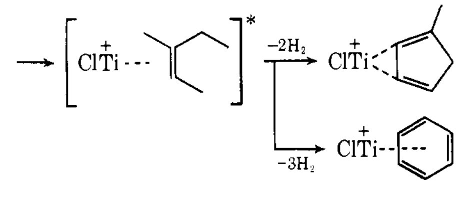


(5)

The reactions of isobutene with these two ions may produce trimethylene-methane complexes.[9,10] The methylpentenes appear to undergo a major rearrangement probably involving cyclization at some point. Reaction schemes consistent with the data are given in (6) and (7).

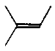
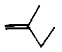
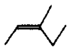
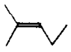


(6)



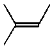
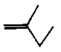
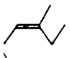
(7)

Table II. Rate Constants[a] for Reactions of $TiCl^+$ with Olefins[b]

| Olefin | Neutral products | | | | | $k_L$[d] |
|---|---|---|---|---|---|---|
| | $3H_2$ | $2H_2$ | $H_2$ | $C_3H_6 + H_2$[c] | $C_2H_4$ | |
|  | | | 5.6 | | | 11.6 |
|  | | | 2.0 | | | 11.6 |
|  | | | 2.2 | | | 12.1 |
|  | | | 3.6 | | | 12.1 |
|  | 4.0 | 4.1 | | | | 12.6 |
|  | 4.4 | 2.5 | | | | 12.6 |
|  | | | | | 1.7 | 12.1 |
|  | 3.8 | 2.6 | 1.3 | | | 12.6 |
|  | | | | 3.1 | | 13.1 |

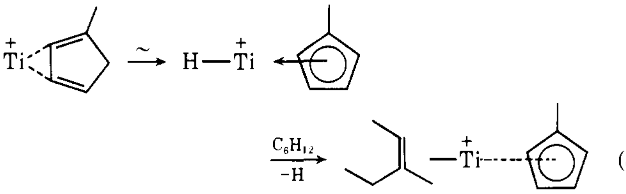
[a] Numbers tabulated are $k \times 10^{10}$ in $cm^3$ $molecule^{-1}$ $s^{-1}$. Uncertainty in the rate constants is ±20% or $\pm 0.5 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, whichever is greater. [b] All reactions are bimolecular dissociative additions involving elimination of the indicated molecules. [c] Or $C_3H_8$. [d] Langevin collision frequency (see ref 14).

Table III. Rate Constants[a] for Reactions of $TiCl_2^+$ with Olefins[b]

| Olefin | Neutral products | | | | $k_L$[c] |
|---|---|---|---|---|---|
| | $H_2 + HCl$ | HCl | $C_3H_6$ | $C_2H_4$ | |
|  | | 3.1 | | | 10.8 |
|  | | 3.6 | | | 10.8 |
|  | | | | | 11.2 |
|  | | 10.0 | | | 11.2 |
|  | 2.1 | 1.8 | | | 11.6 |
|  | 1.3 | 1.1 | | | 11.6 |
|  | | | | 1.7 | 11.2 |
|  | | | 5.6 | | 11.6 |
|  | | | 3.5 | | 12.0 |

[a] Numbers tabulated are $k \times 10^{10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Uncertainty in the rate constants is ±20% or $\pm 0.3 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, whichever is greater. [b] All reactions are bimolecular dissociative additions involving elimination of the indicated molecules. [c] Langevin collision frequency (see ref 14).

The products of (7) are stable to further reaction. The product of (6) reacts according to (2), suggesting the mechanism given in reaction 8. Structures for the products of (6) and (7) such as a hexatriene complex or a cyclic system incorporating the metal cannot be ruled out. We suggest a methylcyclopentadienyl complex as a reasonable product since its formation does not require extensive rearrangement.

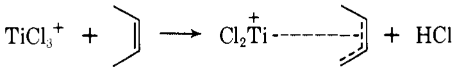


(8)

This tendency to form five-membered rings such as the cyclopentadienyl ring, which can strongly complex with the metal, is encountered frequently in organometallic solution chemistry.[9]

The reactions of $Ti^+$ and $TiCl^+$ with the straight chain olefins are very sensitive to the nature of the olefin. The observed reactions of $TiCl^+$ with 1-pentene and 2-heptene involve carbon–carbon bond cleavage while the observed reactions of $TiCl^+$ with 1-hexene involve elimination of one, two, and three molecules of $H_2$. Thus both the length of the chain and the position of the double bond are important in determining the reaction sequence. The low abundance of $Ti^+$ in the mass spectrum of $TiCl_4$ may have precluded observation of some processes, but $Ti^+$ is evidently less reactive toward the straight chain olefins than $TiCl^+$. The only observed reaction of $Ti^+$ with the straight chain olefins is the elimination of two molecules of $H_2$ from 1-pentene.

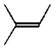
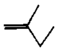
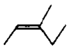
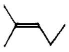
**$TiCl_2^+$ and $TiCl_3^+$ Reactions.** $TiCl_2^+$ and $TiCl_3^+$ have fewer vacancies in their valence shells than do $Ti^+$ and $TiCl^+$. It may also be that the first titanium-chlorine bonds in $TiCl_2^+$ and $TiCl_3^+$ are weaker than that in $TiCl^+$. As a result $TiCl_2^+$ and $TiCl_3^+$ react with the butenes and pentenes to eliminate HCl probably forming a substituted π-allyl complex as indicated in (9).



(9)

These ions react with the straight chain alkenes to cleave carbon–carbon bonds producing smaller olefins. The role of the titanium center in this case may be in some sense the reverse of the role of titanium in the catalytic polymerization of olefins. One of several mechanisms consistent with the data

Table IV. Rate Constants[a] for Reactions of $TiCl_3^+$ with Olefins[b]

| Olefin | Neutral products | | | | | | $k_L$[c] |
|---|---|---|---|---|---|---|---|
| | $H_2$ | HCl | $C_3H_6$ | $C_4H_8$ | $C_5H_{10}$ | "$C_2H_3Cl$" | |
|  | | 7.3 | | | | | 10.4 |
|  | | 5.9 | | | | | 10.4 |
|  | | | | | | | 10.7 |
|  | 1.0 | 6.8 | | | | | 10.7 |
|  | | 2.9 | | | | | 11.0 |
|  | | 1.21 | | | | | 11.0 |
|  | | | 2.52 | | | | 10.7 |
|  | | 0.5 | 0.7 | 5.5 | | 0.3 | 11.0 |
|  | 0.7 | | | 1.4 | 1.4 | | 11.3 |

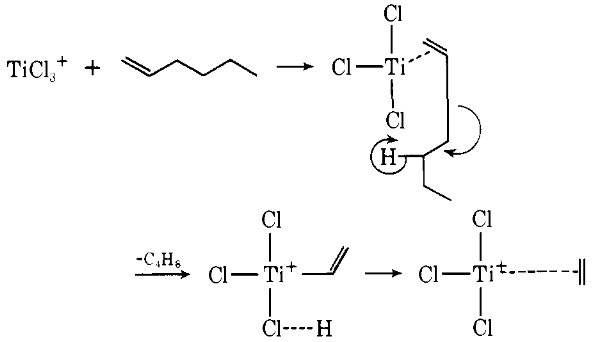
[a] Numbers tabulated are $k \times 10^{10}$ in $cm^3$ $molecule^{-1}$ $s^{-1}$. Uncertainty in the rate constants is ±20% or $\pm 0.2 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, whichever is greater. [b] All reactions are bimolecular dissociative additions involving elimination of the indicated molecules. [c] Langevin collision frequency (see ref 14).

Table V. Limits of Binding Energies between Hydrocarbons and $TiCl_n^+$

| Reaction | Implication[a] |
|---|---|
| $TiCl_3^+$ + 2-heptene → $TiCl_3(C_2H_4)^+$ + 1-pentene | $D(TiCl_3^+-C_2H_4) > 25.2$ |
| $TiCl_3^+$ + 2-heptene → $TiCl_3(C_3H_6)^+$ + 1-butene | $D(TiCl_3^+-C_3H_6) > 22.4$[b] |
| $TiCl_2^+$ + 1-hexene → $TiCl_2(C_3H_6)^+$ + propene | $D(TiCl_2^+-C_3H_6) > 19.4$[b] |
| $TiCl^+$ + 1-pentene → $TiCl(C_3H_6)^+$ + ethylene | $D(TiCl^+-C_3H_6) > 22.2$[b] |
| $TiCl^+$ + *cis*-2-butene → $TiCl(C_4H_6)^+$ + $H_2$ | $D(TiCl^+-C_4H_6) > 28.1$[c] |
| $TiCl^+$ + 1-hexene → $TiCl(C_6H_6)^+$ + $3H_2$ | $D(TiCl^+-C_6H_6) > 29.7$[d] |
| $TiCl^+$ + 2-methyl-2-pentene → $TiCl(C_6H_6)^+$ + $3H_2$ | $D(TiCl^+-C_6H_6) > 35.1$[d] |
| $Ti^+$ + *cis*-2-butene → $Ti(C_4H_6)^+$ + $H_2$ | $D(Ti-C_4H_6)^+ > 28.1$[c] |

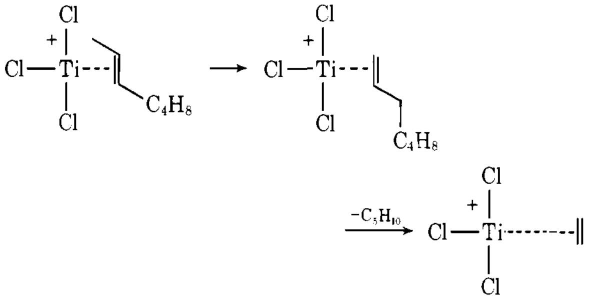
[a] Binding energies in kcal/mol based on hydrocarbon heats of formation derived from group additivities. (S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.) [b] $C_3H_6$ is assummed to be propene. [c] $C_4H_6$ is assumed to be 1,3-butadiene. [d] $C_6H_6$ is assumed to be benzene.

for reaction of 1-hexene and 1-pentene with $TiCl_3^+$ is given in (10).



(10)

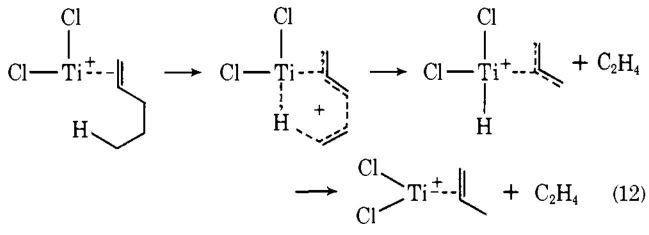
The subsequent displacement of ethylene by 1-hexene or by 1-pentene (reaction 3) substantiates the structure of the product of (10). A similar mechanism may account for the formation of the same neutral product in 2-heptene. Just as important in 2-heptene, however, is a process involving the loss of $C_5H_{10}$ to produce $TiCl_3(C_2H_4)^+$. This latter process could conceivably begin with a 1,3-hydrogen-atom shift as indicated in reaction 11.



(11)

The shift could proceed via a π-allyl hydride intermediate, as is frequently postulated in similar isomerizations of alkenes by metals.[9,11]

$TiCl_2^+$ eliminates only $C_3H_6$ from 1-hexene and 2-heptene, but the ion eliminates only $C_2H_4$ from 1-pentene. This suggests a mechanism that involves cleavage of the bond β-γ to the double bond. Such a mechanism involving initial formation of a donor-acceptor complex between the olefin and the metal is illustrated for 1-pentene by (12). Analogous mechanisms can be envisioned for 1-hexene and 2-heptene.



(12)

1-Hexene displaces $C_3H_6$ from the $TiCl_2C_3H_6^+$ (reaction 4) formed by reaction of $TiCl_2^+$ with 1-hexene. This substantiates that at least when 1-hexene is the reactant the product of (12) has the indicated structure.

An intriguing feature of the reactions of $TiCl_2^+$ and $TiCl_3^+$ is seen from an examination of the rate constants in Tables III and IV. The overall reactivity seems to decrease with increasing substitution of the double bond. The most striking example is that while 2-butene and 2-methyl-1-butene react rapidly with both $TiCl_2^+$ and $TiCl_3^+$, 2-methyl-2-butene does not react at all. This could be the result of a steric effect or some mechanistic consideration. The branched alkenes are generally somewhat more stable thermodynamically than their unbranched isomers. This could play a role in their stability to attack by the $TiCl_n^+$ ions.

**Thermochemistry.** As indicated in Tables I-IV the observed reactions generally have rates within an order of magnitude of the reactant collision frequencies[14] and hence are thermoneutral or exothermic. The reactions therefore imply lower limits on the binding energies between various hydrocarbons and the $TiCl_n^+$ ions. Several of these limits are listed in Table V. In determining the limits it is necessary to assign structures to the hydrocarbon ligand in the metal complex product ion and to the neutral products. The structures assigned are those of the most stable hydrocarbon consistent with all the chemistry observed and reasonably simple mechanisms. In general, choosing other structures gives greater lower limits. The possibility of using competitive ligand substitution[12,13] reactions to obtain relative metal ligand bond strengths in these systems is under investigation in our laboratory.

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## References and Notes

(1) H. Uelzmann, *J. Org. Chem.*, **25,** 671 (1960).
(2) P. Cossee and E. J. Arlman, *J. Catal.*, **3,** 80 (1964).
(3) H. Roehl, E. Lange, T. Golsal, and G. Roth, *Angew. Chem.*, **74,** 155 (1962).
(4) J. D. Baldeschweiler, *Science*, **159,** 263 (1968).
(5) D. P. Ridge, *J. Am. Chem. Soc.*, **97,** 5670 (1975).
(6) M. B. Comisarow, *J. Chem. Phys.*, **55,** 205 (1971).
(7) R. W. Kiser, J. G. Dillard, and D. L. Dugger, *Adv. Chem. Ser.*, **No. 72,** 153 (1968).
(8) J. Müller and W. Gole, *Chem. Ber.*, **106,** 1129 (1973).
(9) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974.
(10) J. S. Ward and R. Pettit, *Chem. Commun.*, 1419 (1970); K. Ehrlich and G. F. Emerson, *ibid.*, 59 (1969).
(11) R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc. A*, 353 (1970).
(12) G. H. Weddle, J. Allison, and D. P. Ridge, *J. Am. Chem. Soc.*, in press.
(13) R. R. Corderman and J. L. Beauchamp, private communication.
(14) W. C. Gardiner, Jr., "Rates and Mechanisms of Chemical Reactions", W. A. Benjamin, Menlo Park, Calif., 1972, p 76.

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# Negative Activation Enthalpy in the Dimerization of Anthracene at Very High Pressure

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**Abstract:** Solid polycrystalline anthracene polymerizes more readily at 80 K (liquid nitrogen cooling) than at room temperature when subjected to 58 000 bars of quasihydrostatic pressure in a piston-cylinder device. The products appear to be four dimers. Three of the four show accelerated rate effects if the anthracene was previously irradiated with $^{60}Co$ $\gamma$ radiation. It is postulated that the negative temperature coefficient can be rationalized if the compressionally derived activation energy $P\Delta V^{\ddagger}$ exceeds the thermal activation energy $\Delta E^{\ddagger}$.

Polycyclic aromatic hydrocarbons are in general strongly affected by very high pressures in excess of 10 kbars. Shifts in band maxima may be observed in the ultraviolet, visible, and fluorescent spectra of such materials under these extreme conditions. The magnitude of this effect indicates that the application of high pressure results in a significant perturbation of the intramolecular potential function. The variation in electrical resistivity with pressure of many such semiconducting organic solids has been investigated in order to attempt to quantitate this phenomena. In particular Drickamer et al.,[1-4] Vaidya and Kennedy,[5] and others[6-8] have measured the physical effects of compressing organic materials to pressures as high as 500 kbars.

We report here a study of the chemical effects of very high pressures upon the polycyclic aromatic hydrocarbon anthracene. Previously little attention has been paid to the chemical reactions which are greatly accelerated by such conditions. This area is of critical importance as the variations in physical properties which are measured will be significantly modified by even a small total amount of self-reaction. In addition the composition and quantity of the products provides information as to the general mechanism of reaction in the organic solid state and indirectly may shed some light on the nature of the intermolecular forces which are responsible for the many unique properties of these materials.

## Experimental Section

Anthracene (zone refined, 99.9+%, Aldrich Chemical Co.) was transferred in a nitrogen or argon filled glove box to a cylindrical sample capsule of either tantalum or Teflon of outside dimensions 1.00 in. by 0.250 in. The filled capsule was placed inside a graphite and talc sleeve which could be wrapped in lead foil and fitted into a cylindrical high-pressure vessel of tungsten carbide compact (Carmet Grade CA-4). The open end of the sample vessel was closed with a carbide end plug, separated by a thin steel shim. All carbide components were massively supported (along the horizontal axis) with tool steel interference fitted binding rings. The general design of the press and sample assembly is described in detail elsewhere[9] and is similar to that of Kennedy and LaMori[10] and Katzman.[11]

Sample temperatures were monitored with the aid of a platinum: platinum, 10% iridium thermocouple which was inserted through a capillary hole in the carbide end plug. Pressure was calculated from the master ram Heise gauge reading using area and frictional corrections. Cooling to 80 K was effected by an external liquid nitrogen jacket placed about the steel support rings of the sample vessel.

Analysis of the sample after removal of pressure was carried out using both conventional and chemical ionization mass spectrometry.[12,13] Unpressurized starting material was used as an internal control. Inlet temperature and pressure were standardized from analysis to analysis in order to eliminate possible interferences from contaminants which might be formed in situ.

$\gamma$ irradiation was performed with a kilocurie $^{60}Co$ source at the U.C.L.A. Laboratory for Radiobiology and Nuclear Medicine. This