culations have led to a new understanding of the mechanism of cyclopropane ring openings by palladium(II), and it is found that exactly the opposite to what was previously thought is true. The conclusion is that corner activation is the favored pathway, especially when the metal has the possibility to ionize into a cationic complex. Instead it is the edge pathway that needs special circumstances to become available.

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Registry No. C_3H_6, 75-19-4; $PdCl_2$, 7647-10-1; $PdCl_4$, 14349-67-8; $PdCl^+$, 19651-81-1.

Rate Constant for Cyclization/Decyclization of the Phenyl Radical

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Abstract: Formation of cyclic C_6H_5 from $^\bullet CH{=}CH{-}CH{=}CH{-}C{\equiv}CH$ was investigated by means of the MINDO/3 parametrization of SCF-MO theory and RRKM calculations of the unimolecular rate constants for both directions of reaction.

We report a theoretical study of the formation of phenyl radical by attack of a terminal vinyl radical upon a terminal ethynyl group (Figure 1), a reaction of importance in soot nucleation.[1]

Procedure

Structures and energies were computed by the MINDO/3 method with the MOPAC programs.[2] Standard MOPAC options were used for locating the transition structure[3] and for computing force constants and vibrational frequencies. No constraints were used except for imposing planarity on the phenyl radical.

Rate constants for unimolecular isomerizations require an extension of standard RRKM theory.[4] For incorporation into a modeling program the conversion from the open-chain radical (OC) to the phenyl radical (PR) has to be described by a kinetic equation

$$-\frac{\mathrm{d[OC]}}{\mathrm{d}t} = k_\mathrm{f}[\mathrm{OC}] - k_\mathrm{r}[\mathrm{PR}] \qquad (1)$$

The corresponding formulation of the unimolecular process is written

$$\mathrm{OC} \underset{k_{-1}[\mathrm{M}]}{\overset{k_1[\mathrm{M}]}{\rightleftarrows}} \mathrm{OC}^* \underset{k'(E)}{\overset{k(E)}{\rightleftarrows}} \mathrm{PR}^* \underset{k'[\mathrm{M}]}{\overset{k'_{-1}[\mathrm{M}]}{\rightleftarrows}} \mathrm{PR} \qquad (2)$$

and the expression for k_f is

$$k_\mathrm{f} = \int_{E_0}^{\infty} \frac{B(E)k(E)\,\mathrm{d}E}{1 + \dfrac{k(E)}{k_{-1}[\mathrm{M}]} + \dfrac{k'(E)}{k'_{-1}[\mathrm{M}]}} \qquad (3)$$

where $B(E)$ is the Boltzmann distribution of molecules and $k(E)$ is the RRKM energy dependent unimolecular rate constant.

Table I. Molecular Properties Computed by the MINDO/3 Method

Hexa-1,3-dien-5-yn-yl radical								
Standard Enthalpy of Formation: 116.8 kcal/mol								
Moments of Inertia:[a] A = 117.7, B = 356.6, C = 474.3								
Vibration Frequencies[b]								
72	111	252	253	424	415	593	616	677
692	710	760	796	844	957	1089	1131	1184
1352	1584	1720	2311	3275	3421	3440	3640	3795
Phenyl Radical								
Standard Enthalpy of Formation: 69.6 kcal/mol								
Moments of Inertia: A = 134.9, B = 153.6, C = 288.4								
Vibration Frequencies								
372	408	523	552	558	682	782	805	827
840	849	1031	1045	1089	1092	1152	1154	1238
1442	1457	1589	1686	3477	3484	3497	3518	3521
Transition Structure								
Standard Enthalpy of Formation: 133.4 kcal/mol								
Moments of Inertia: A = 149.6, B = 183.1, C = 332.7								
Vibration Frequencies								
−424[c]	230	301	308	440	462	613	666	682
717	750	765	823	866	1047	1080	1094	1171
1362	1456	1644	2057	3374	3475	3512	3582	3732

[a] Units g cm^2 × 10^{40}. [b] Units cm^{-1}. [c] Reaction coordinate.

Direct counts of densities and numbers of states were used for computing $k(E)$ from the MINDO/3 vibrational frequencies. The path degeneracy is 1 for isomerization of OC and 2 for isomerization of PR. Collision diameters were taken to be 0.53 nm for OC and PR and 0.34 nm for M, as estimates appropriate to reaction in Ar buffer gas; the corresponding collision diameter for PR–Ar and OC–Ar collisions is then

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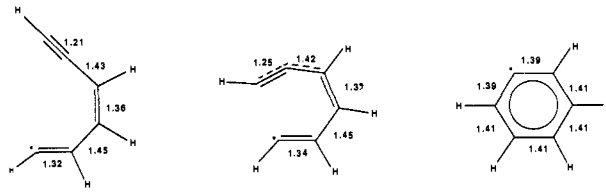

Figure 1. Computed structures for open chain, transition structure, and phenyl radicals.

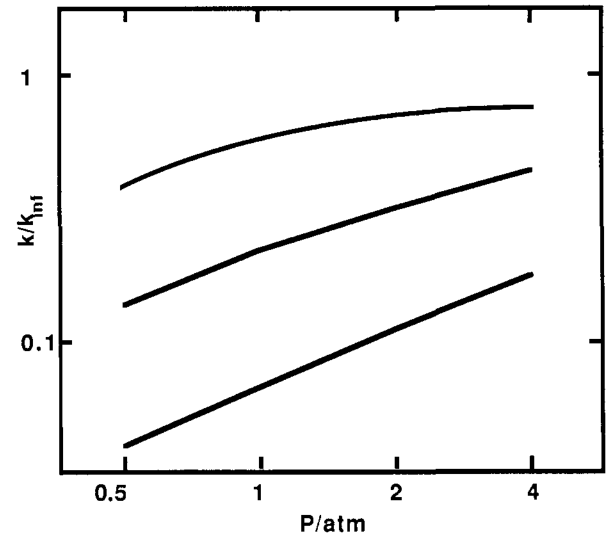

Figure 2. Falloff of unimolecular rate constant at 1500 (upper), 2000, and 2500 K.

0.43 nm. The remaining molecular properties were taken from the MINDO/3 calculations.

Results and Discussion

The structures computed by MINDO/3 for the three species of interest are shown in Figure 1. Molecular properties are given in Table I. Except for the heats of formation, discussed below, the molecular properties are unremarkable. The low-frequency vibrational modes of the open-chain radical were treated as true vibrations in the rate constant calculation even though they are clearly reflecting the presence of an essentially free rotation.

The unimolecular rate constants computed for 1500, 2000, and 2500 K are shown for a range of pressures in Table II and Figure 2. For the temperature and pressure range of shock-tube experiments on soot formation in C_2H_2–Ar mixtures the computed rate constants are about an order of magnitude lower than the 10^{10} s^{-1} value used in simulations.[1] This difference would change the computed soot yield values by no more than a factor somewhere between 2 and 4 for pyrolysis of acetylene, depending on the thermochemical data adopted, less for other pyrolytic soot sources, and far less in an oxidizing environment. The falloff curves (Figure 2) are typical for molecules of this size for these conditions.[5]

Because of the high degree of reversibility within the soot-forming reactions, equilibrium constants prove to be more important than rate constants in determining the course of reaction. Equilibrium constants for use in computer simulations were computed with thermochemical data derived from group-additivity estimates.[6] For the parametrization used these implied enthalpy changes of 112 kcal/mol for removal of an H atom from benzene and 48 kcal/mol for opening the phenyl ring compared to the MINDO/3 values of 93 and 47 kcal/mol, respectively. It is of interest to inquire as to the source of the large difference in the C–H bond dissociation energy. The MINDO/3 value for the standard enthalpy of formation of phenyl radical (70 kcal/mol) indicates greater stability than the experimental values of 78, 80, and 81 kcal/mol derived from kinetics experiments[7-9] and 83 kcal/mol derived from mass-spectrometric studies.[10,11] The only other theoretical value of which we are aware is the BAC-MP4 result of 88 kcal/mol.[12] For benzene itself, MINDO/3 overestimates the standard enthalpy of formation, experimentally 20 kcal/mol, by 9 kcal.[2] The apparently low C–H bond dissociation energy thus arises from an unusually large positive discrepancy in the MINDO/3 standard enthalpy of formation of benzene combined with an apparently low value for phenyl radical. In view of the uncertain experimental value[7-11] it is clear that further theoretical and experimental study is justified. In computing the molecular properties in this study we had elected not to use the MNDO parametrization because of its known tendency to overestimate barriers to breaking C–C bonds.[13] After the rate constant calculations had been completed we were in a position to repeat the molecular properties calculation with the AM-1 parametrization, which gives the standard enthalpy of formation of benzene only 2 kcal/mol high. The computed enthalpies of formation of the open-chain radical, phenyl radical, and the transition structure proved to be 127, 73, and 146 kcal/mol, respectively, with essentially identical geometries as computed by MINDO/3. This value for phenyl radical then implies an AM-1 value for the C–H bond dissociation energy in benzene of 103 kcal/mol, 10 kcal/mol above the MINDO/3 value. A C–H bond dissociation energy lower than the 112 kcal/mol value used in the simulations would imply lower activation energies for H abstraction from aromatic rings and thus increase computed soot yields. The higher relative stability of phenyl radical compared to the open chain radical (54 kcal/mol for AM-1 compared to 47 kcal/mol for MINDO/3) would, extended by analogy to the higher ring radicals, also increase computed soot yields.

Table II. Unimolecular Rate Constants

P^a	$k(PR \rightarrow OC)^b$	$k(OC \rightarrow PR)^b$	k/k_∞	order	$\langle E \rangle^c$
1500 K; $\langle E \rangle$ of Energized Molecules = 1.03×10^4; $K_{eq}(OC \rightarrow PR) = 1800$					
380	1.6×10^5	2.9×10^8	0.42		1.32×10^4
760	2.1×10^5	3.8×10^8	0.55	1.39	1.38×10^4
1520	2.6×10^5	4.7×10^8	0.68	1.29	1.43×10^4
3040	3.0×10^5	5.4×10^8	0.79	1.21	1.48×10^4
∞	3.8×10^5	6.9×10^8	1.0	1	1.59×10^4
2000 K; $\langle E \rangle$ of Energized Molecules = 1.83×10^4; $K_{eq}(OC \rightarrow PR) = 26$					
380	1.5×10^7	3.8×10^8	0.14		1.77×10^4
760	2.3×10^7	6.0×10^8	0.22	1.64	1.85×10^4
1520	3.4×10^7	8.7×10^8	0.32	1.55	1.92×10^4
3040	4.6×10^7	1.2×10^9	0.44	1.45	2.01×10^4
∞	1.1×10^8	2.7×10^9	1.0	1	2.4×10^4
2500 K; $\langle E \rangle$ of Energized Molecules = 2.09×10^4; $K_{eq}(OC \rightarrow PR) = 2.1$					
380	1.2×10^8	2.5×10^8	0.04		2.29×10^4
760	2.1×10^8	4.4×10^8	0.07	1.81	2.36×10^4
1520	$o.5 \times 10^8$	7.3×10^8	0.12	1.74	2.45×10^4
3040	5.6×10^8	1.2×10^9	0.19	1.66	2.55×10^4
∞	3.0×10^9	6.2×10^9	1.0	1	3.3×10^4

[a] Units Torr. [b] Units s^{-1}. [c] Units cm^{-1}.

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