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Ab initio SCF MO Study of the Gas-Phase Reaction $C_6H_6 + CH_3 \rightarrow C_6H_5(CH_3)H \rightarrow C_6H_5CH_3 + H$

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The minimum-energy paths for a sequence of reactions $C_6H_6 + CH_3 \rightarrow C_6H_5(CH_3)H \rightarrow C_6H_5CH_3 + H$ have been traced by the UHF SCF procedure employing the 4-31G basis functions, to locate the transition states. The activation barrier heights obtained are well in accord with the available gas-kinetic data.

The addition reactions of the hydrogen atom[1)] and the methyl radical[2)] to olefins and aromatics form an important class of elementary reactions, inasmuch as they provide fundamental kinetic data manifesting the radical reactivities of unsaturated compounds. Energetics as well as the kinetics of these reactions deserves rigorous tests according to the least empirical theoretical formalisms possible. Ethylene[3,4)] and benzene in particular as the prototypes of unsaturated compounds are the most fundamental in this regard.

We here wish to report the ergodography of the sequence of reactions

$$C_6H_6 + CH_3 \xrightarrow{1} C_6H_5(CH_3)H \xrightarrow{2} C_6H_5CH_3 + H \qquad (1)$$

investigated by the unrestricted Hartree-Fock (UHF) SCF procedure employing the 4-31G basis functions.[5)] The same issue has already been dealt with by Amano et al.[6,7)] on an approximate semiempirical level. Our strategy now is to let the treatments be based on full geometry optimizations of all the stationary points, to evaluate the activation barrier heights in a much greater confidence.

SCF calculations were carried out using the Gaussian-70 program.[8)] The conventional split-valence 4-31G basis sets[5)] are adopted as the basis atomic-orbital functions. For the methyl radical and benzene, the SCF optimized geometries are used: $CH_3(D_{3h})$, r_{CH} = 0.10702 nm, and E_{UHF} = -39.50498 hartree ; $C_6H_6(D_{6h})$, r_{CC} = 0.13840 nm, r_{CH} = 0.10721 nm, and E_{RHF} = -230.37783 hartree. Full geometry optimization was carried out for the adduct radical. The minimum-energy paths for reactions were traced by choosing the distance R between the incoming methyl carbon atom (or the outgoing hydrogen atom) and the reaction-site carbon atom of benzene as the principal reaction coordinate. The phenyl group was assumed to be planar throughout the course of reaction.

For the purpose of preliminary tests, we have studied the hydrogen atom addition to benzene

$$C_6H_6 + H \longrightarrow C_6H_7 \qquad (2)$$

The reaction is found to proceed by maintaining the C_s' symmetry. The product radical takes the C_{2v} symmetry. Its optimized structure is shown in Fig. 1(A). The energy change of reaction is calculated to be $\Delta E = -122.2$ kJ/mol.

Geometry of the transition state located is shown in Fig. 1(B). The activation barrier height obtained is $\Delta E^\ddagger = 13.4$ kJ/mol, in good agreement with the experimental activation energy $E_a = 16$ kJ/mol determined for the gas-phase reaction.[9] Although no vibrational zero-point energy corrections have been made, the SCF procedure adopted seems to be sufficiently reliable for use in theoretical considerations of the reactivity of benzene to radicals.

The minimum-energy paths of the reaction sequence (1) have been traced, assuming that the entire reacting system maintains the C_s' symmetry with respect to the plane (σ') which contains the phenyl carbon atoms C^1 and C^4 and is perpendicular to the plane (σ) of the phenyl group (Fig. 2). The methyl carbon atom (C^{13}) and the hydrogen atom (H^{12}) attached to the reaction-site carbon atom (C^1) are therefore both assumed to lie on the symmetry plane σ'. The geometry parameters of the structures optimized for the adduct radical $C_6H_5(CH_3)H$, the transition states TS1 and TS2 of the initial bimolecular reaction (step 1) and the subsequent unimolecular C-H bond cleavage (step 2), respectively, and toluene $C_6H_5CH_3$ as the final product are summarized in Table 1. It is confirmed by a separate geometry optimization that the C_s conformation of toluene which is symmetric with respect to the phenyl plane (σ) is no more stable than the C_s' structure (Table 1) symmetric with respect to the perpendicular plane (σ'). In other words, there is virtually no energy barrier (< 0.05 kJ/mol) for the internal rotation of the methyl group.

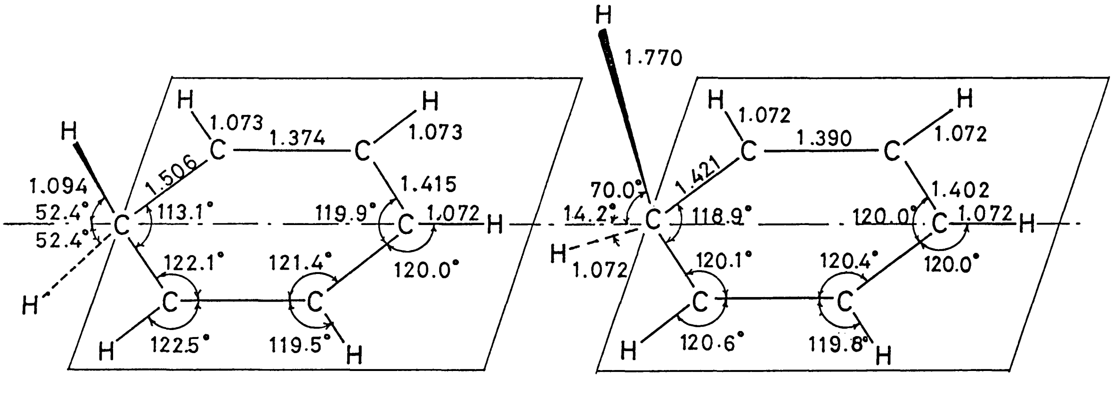

Fig. 1. Geometries optimized for the adduct radical and the transition state for the reaction $C_6H_6 + H \longrightarrow C_6H_7$.

Figure 3 diagrammatically illustrates the potential energy changes calculated for the entire process of reaction (1). Step 1, i. e., the methyl radical addition to benzene, has the barrier height $\Delta E^{\ddagger}$ = 51.8 kJ/mol and the energy change of reaction ΔE = -47.3 kJ/mol. For step 2, i. e., the hydrogen detachment from the radical giving rise to toluene, we have $\Delta E^{\ddagger}$ = 136.1 kJ/mol and ΔE =116.3 kJ/mol. For the overall process, the net energy change calculated is therefore ΔE = 69.0 kJ/mol. All these values may well be affected to some extent by the vibrational energy corrections, however.

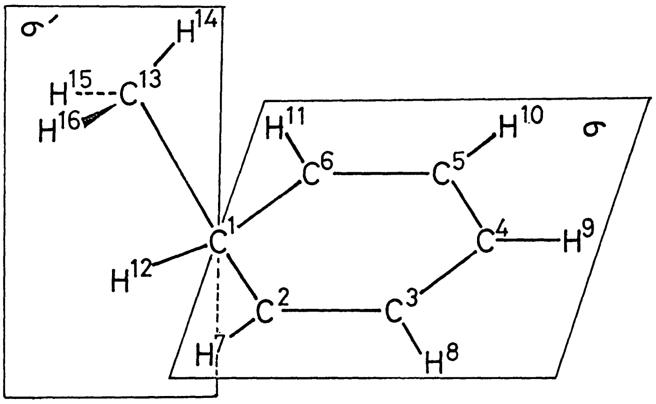

Fig. 2. Spatial arrangement (C_s') and the labeling of the atoms involved in the reaction $C_6H_6 + CH_3 \longrightarrow C_6H_5(CH_3)H \longrightarrow C_6H_5CH_3 + H$.

Table 1. Optimized Geometries[a)]

		TS1	$C_6H_5(CH_3)H$	TS2	$C_6H_5CH_3$ + H
Energy/hartree	E + 269	-0.86308	-0.90081	-0.84898	-0.85649
Bond lengths/nm	C^1C^2	0.1436	0.1509	0.1428	0.1388
	C^2C^3	0.1388	0.1374	0.1390	0.1383
	C^3C^4	0.1405	0.1414	0.1401	0.1383
	$H^{12}C^1$	0.1073	0.1093	0.1768	———
	$C^{13}C^1$	0.2107	0.1545	0.1516	0.1509
	$H^{14}C^{13}$	0.1074	0.1083	0.1085	0.1085
	$H^{15}C^{13}$	0.1076	0.1083	0.1081	0.1082
Bond angles/°	$C^2C^1C^6$	117.4	112.1	117.2	118.3
	$C^3C^2C^1$	120.8	122.8	121.1	120.9
	$C^4C^3C^2$	120.6	121.3	120.5	120.2
	$C^5C^4C^3$	119.7	119.7	119.6	119.4
	$H^{12}C^1C^4$	157.0	123.8	103.9	———
	$C^{13}C^1C^4$	114.0	129.7	163.2	180.0
	$H^{14}C^{13}C^1$	102.9	110.5	109.9	111.1
	$H^{15}C^{13}C^1$	103.4	110.7	111.4	111.3
Dihedral angle/°	$H^{15}C^{13}C^1H^{14}$	119.9	119.9	119.6	119.9

a) The bond lengths and angles associated with the o-, m-, and p-hydrogens are all omitted here.

The reverse process of step 2, i. e., the hydrogen atom addition to toluene at the ipso position, is predicted to have the barrier height $\Delta E^{\ddagger}$ = 19.8 kJ/mol. Since TS2 is no doubt higher in energy than TS1, the hot radical formed should be liable to decompose spontaneously into benzene and the methyl radical, in harmony with the view presented by Amano and his collaborators.[6,10,11] The barrier height of 19.8 kJ/mol here obtained agrees well with the height 20 kJ/mol, which has been deduced experimentally.[6]

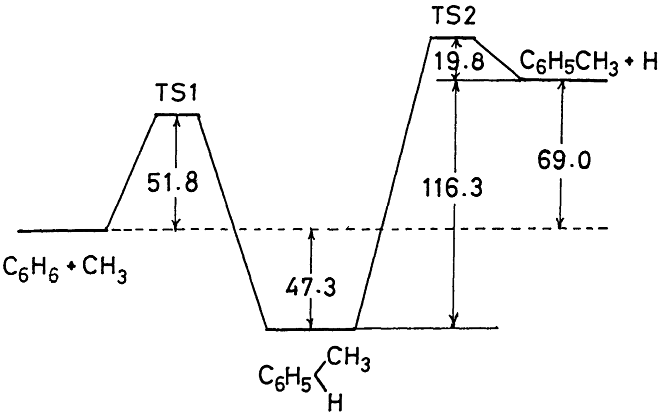

Fig. 3. Potential energy diagram calculated for C_6H_6 + CH_3 $\rightarrow$ $C_6H_5(CH_3)H$ $\rightarrow$ $C_6H_5CH_3$ + H. The energy level gaps shown are in units of kJ/mol.

The SCF calculations using the 4-31G basis set thus provide reliable estimates of the barrier heights for the reactions C_6H_6 + H $\rightarrow$ C_6H_7 and C_6H_6 + CH_3 $\rightarrow$ $C_6H_5(CH_3)H$ $\rightarrow$ $C_6H_5CH_3$ + H. More rigorously, however, dependences of the results on the size of the basis set used would have to be examined. Effects of electron correlations may also be an influencing factor. The present treatments should therefore be regarded merely as a practical compromise between accuracy and labor.

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