Quantum Chemical Calculations for some Toluene Derivatives

Ewa Broclawik and Malgorzata Witko
Institute of Catalysis and Surface Chemistry,
Polish Academy of Sciences, Cracow, Poland

Z. Naturforsch. **43a,** 823–824 (1988);
received May 3, 1988

Heterogeneous catalytic oxidation of p-substituted toluenes is of interest [1] for the production of derivatives of benzaldehyde, some of which (e.g. anisic aldehyde and p-tert-butylbenzaldehyde) being valuable components of fragrances. The mode of the adsorption depends on the type of the hydrocarbon and the active center on the catalyst surface. In order to elucidate the mechanism of the reaction it is necessary to know the electronic and geometrical properties of the molecule to be adsorbed, since the geometry of the adsorption complex should decide about which of the many possible routes of transformation of the complex during the oxidation predominates, and hence about the selectivity of the reaction.

Having these factors in mind, quantum chemical calculations were carried out by means of a semiempirical MNDO method with automatic geometry optimization in order to investigate the electronic structure of toluene and the influence of various substituents on the electronic properties and charge distribution. Semiempirical methods based on ZDO approximation have been widely used in quantum chemical calculations. Among them, the MNDO method often gives more appropriate results than those obtained by ab initio methods, probably because of the inclusion of correlation effects through parameters.

The calculations were performed for neutral molecules and doubly charged cations of a series of p-substituted toluenes which comprise toluene, p-xylene, p-chlorotoluene, p-nitrotoluene and p-methoxytoluene. The results are presented in Table 1, in which the charge distributions as well as selected bond distances in various fragments are given.

Discussion

In the case of the neutral molecules, substitution influences mainly the aromatic ring, the charge and bond distances in the CH_3 group remaining almost unchanged. For toluene and p-xylene the aromatic nucleus bears negative charge, whereas for the other compounds it is positive, with the

Table 1. Charge distribution and optimized structural parameters of toluene derivatives.

	Toluene	p-xylene	p-chloro-toluene	p-nitro-toluene	p-methoxy-toluene
			neutral molecule		
q_{Ar}*	−0.128	−0.138	0.034	0.110	0.042
π_{Ar}	−0.005	−0.011	−0.030	0.020	−0.037
q_{CH_3}	0.069	0.069	0.078	0.088	0.071
$q_H(CH_3)$	−0.005	−0.005	−0.001	0.005	−0.005
	−0.002	−0.001	0.002	0.011	0.000
q_{subst}**	0.059	0.069	−0.012	−0.198	−0.113
		C 0.080		N 0.486	O −0.305
		H −0.005		O −0.342	C 0.221
$R_{CH}(CH_3)$	1.110	1.110	1.110	1.110	1.110
R_{Ar-CH_3}	1.506	1.505	1.506	1.507	1.506
			cation 2+		
q_{Ar}*	1.453	1.338	1.338	1.446	1.367
π_{Ar}	1.797	1.664	1.551	1.794	1.326
q_{CH_3}	0.365	0.331	0.338	0.380	0.287
$q_H(CH_3)$	0.130	0.120	0.120	0.140	0.000
	0.190	0.170	0.180	0.200	0.140
q_{subst}**	0.182	0.331	0.325	0.152	0.364
$R_{CH}(CH_3)$	1.122	1.119	1.120	1.123	1.116
R_{Ar-CH_3}	1.466	1.473	1.473	1.463	1.485

* the aromatic nucleus (Ar) was built from the benzene ring and two pairs of hydrogen atoms in meta and ortho position with respect to the CH_3 group.
** H, CH_3, Cl, NO_2 and OCH_3 were taken as substituents, respectively.

Reprint requests to Dr. M. Witko, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences ul. Niezapominajek, P-30-239 Cracow/Polen.

0932-0784 / 88 / 0800-0823 $ 01.30/0. – Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

largest positive charge in the case of p-nitrotoluene. As for the π-electrons, only the NO_2 group is a π-electron acceptor (second order substituent); the other groups appear to be first order substituents and donate π-electrons to the ring.

There are two factors which are likely to influence the bonding of the organic molecule to the surface active center: the π-electron distribution on the benzene ring and the value of the negative charge on the substituent. In the case of toluene and p-xylene the substituents are positively charged, and therefore bonding with the acceptor active center will occur via the aromatic ring. In the case of the remaining molecules the substituent group is more negative than the benzene ring, and so bonding via the chlorine or oxygen atom will be favoured.

For the positively charged molecules the charge distribution and geometrical structure are more sensitive to the type of substituent. For toluene and p-xylene the largest changes in the total charge on passing from neutral to $+2$ charged molecules occur for the aromatic nucleus. For the other compounds the most significant changes in charge occur in the substituent group.

The charge on the methyl group differs for different molecular cations, being most positive for p-nitrotoluene and least positive for methoxytoluene. At the same time the charge on the hydrogen atoms in the CH_3 group becomes positive, which should facilitate the abstraction of this atom by an O^{2-} ion, frequently postulated as one of the steps in activation of hydrocarbons in their oxidation to aldehyde [2].

The bond between the CH_3 group and the aromatic ring is for all the cations shortened (the smallest effect occurs for methoxytoluene). The bond distance between the substituent and the aromatic nucleus is most significantly shortened for methoxytoluene cation, where there is also the largest change in the charge distribution on the methoxy group.

In catalytic reactions, the step of adsorption is usually the most important one. One can take the negative charge (total or π-part) on the ring or substituent (depending on the mode of adsorption) as the measure of the bonding ability. Thus one can postulate the following ordering of the studied molecules according to their adsorption ability: nitro-, methoxy-, chlorotoluene, p-xylene, toluene.

The catalytic oxidation of toluene, p-tertbutylotoluene and methoxytoluene on various mixed oxide systems has been studied experimentally [1, 3]. The methoxy derivative was found to be the most active one, p-tertbutylotoluene showed a smaller activity and toluene the smallest one. These experimental results are consistent with the presented calculations provided p-xylene can be taken as corresponding to p-tertbutylotoluene. Indeed, according to the calculations p-methoxytoluene is considerably different from the two other experimentally studied species. A behaviour similar to that of methoxytoluene could be suggested for chloro- and nitrotoluene.

Acknowledgements

The work was partly supported by the Institute of Low Temperature, Polish Academy of Sciences, Wroclaw, Poland.

[1] B. Grzybowska, M. Czerwenko, and J. Sloczynski, Catal. Today, **1,** 157 (1987)
[2] J. Haber, and M. Witko, Acc. Chem. Research **14,** 1 (1981)
[3] M. Czerwenko, B. Grzybowska, and M. Gasior, Bull. Pol. Acad. Sci. **35,** 353 (1987)