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MNDO calculations on the reactivity of furan compounds towards polymeric radicals

José A. Paz, Jacques Rieumont*, Luis A. Montero and J. Raúl Alvarez
Faculty of Chemistry, University of Havana, Havana 10400, Cuba
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The semiempirical self-consistant field / modified neglect of differential overlap (SCF-MNDO) method has been used to calculate the energies of the highest occupied, lowest unoccupied and singly occupied molecular orbitals (HOMO, LUMO and SOMO) of some neutral furan-derivative molecules and their radical formed by addition of a dimeric vinyl acetate radical to the furan ring. Molecules with lower energy of the HOMO and LUMO behave as stronger retarders. This suggests an interaction with the attacking radical of the type SOMO–LUMO giving a more stabilized radical with lower SOMO energy. The rate of retarded radical polymerization of vinyl acetate in the presence of some furan compounds shows a good correlation with several sets of reactivity substituent constants and with the dipole moment obtained by quantum-mechanical calculations. However, the calculated enthalpies are low or positive and do not correlate. Besides, values of the reactivity substituent constants are suggested as 0.27 for the $-CH_2-NH_2$ side group and 0.74 for $-CONH_2$.

(Keywords: furan compounds; molecular-orbital calculations; reactivity correlations)

INTRODUCTION

Furan compounds behave as retarders or inhibitors of the radical polymerization of common monomers[1]. The site of addition of macroradicals to the furan ring has been experimentally established to be related to its carbon C5. Furthermore, an allylic-type radical has been suggested to be the radical species formed[2]. Recently, theoretical support has been added to this view by using the MNDO (modified neglect of differential overlap) technique[3].

To our knowledge the structure and reactivity of these compounds towards polymeric radicals have not been thoroughly considered theoretically or experimentally up to now. In order to accomplish this task, the retarding effect of some furan compounds on the radical polymerization of vinyl acetate was correlated. Rate measurements were compared with the reactivity constants for the substituents and with some electronic and molecular properties obtained by semiempirical self-consistant field (SCF) MNDO quantum-mechanical calculations.

METHOD OF CALCULATION

The semiempirical SCF-MNDO[4] procedure has been used to calculate the electronic energy of all radicals and molecules. The optimum molecular geometry has been found by the Davidson–Fletcher–Powell[5] gradient method, in each case looking for the minimum in the energy hypersurface with respect to all atomic coordinates in all molecules. Calculations and molecular graphics have been obtained by the TC-Habana package[6] of programs for theoretical chemistry on personal computers. This kind of calculation is parametrized for heats of formation in the minimal SCF geometry at 298 K. It means that only the enthalpic changes of the isolated molecules are taken into account.

RESULTS AND DISCUSSION

Hammett-type plots

The logarithms of the vinyl acetate initial rates of polymerization (R_{p0}) in the presence of some furan compounds[6] were plotted *versus* different sets of reactivity substituent constants compiled by Jaffe and Swain: σ_p and σ_p^c (ref. 8) and σ_p^+ (ref. 9).

In *Table 1* the furan compounds are listed according to their decreasing retardation power. Thus, R_{p0} is inversely proportional, indicating the stabilizing effect of the side group on the radical formed by addition to the furan ring. Good correlations are observed in each case, although not all substituent constants are available. The best correlation coefficient was obtained with σ_p^c and this permits one to estimate the values for CH_2NH_2 ($\sigma_p^c = 0.27$) and for $CONH_2$ ($\sigma_p^c = 0.74$) not found in the literature consulted. These estimations must be verified by other methods.

The furan compounds have two main differences in comparison with the aromatic series. The retarding effect is more pronounced and the species with donor groups are weaker than furan itself as retarders. This could be verified from *Tables 1* and *2*. One can see the higher values of the characteristic transfer constants (C_s) (the

* To whom correspondence should be addressed

Table 1 Relationship between the initial rate of retarded radical polymerization (R_{p0}) of vinyl acetate in the presence of some furan compounds and several sets of reactivity substituent constants[a]

Furan side group	$R_{p0} \times 10^5$ (mol l^{-1} s^{-1})	Reactivity substituent constants		
		σ_p	σ_p^c	σ_p^+
-CHO	4	0.22	1.103	
-$COCH_3$	9	0.52	0.874	0.57
-$CONH_2$	14	0.28		
-COOH	15	0.27	0.728	0.47
-CH_2NH_2	30			
-CH_2OH	37		0.08	
-H	39	0	0	0
-CH_3	44	−0.17	−0.17	−0.26
Correlation coefficient		−0.983	−0.984	−0.964

[a] Vinyl acetate = 8.65 mol l^{-1}; retarder = 0.003 mol l^{-1}; AIBN = 0.005 mol l^{-1}; temperature = 60°C

Table 2 Characteristic transfer constants in the radical polymerization of vinyl acetate at 60°C for the aromatic and furan series

Furan side group	Constant $C_s \times 10^4$	
	Aromatic[a]	Furan[b]
-CHO	540	20860
-$COCH_3$	100	11300
-COOH	50	7300
-CH_2OH	556[c]	2500
-H	1.2	2200
-CH_3	21.6	2100
-OCH_3	10	

[a] From ref. 16
[b] From ref. 7
[c] At 70°C

ratio of transfer kinetic constant to propagation) for the furan derivatives and that 2-methylfuran is weaker than furan while toluene is stronger than benzene. Unfortunately 2-methoxyfuran is not stable enough to complete *Table 2*. In fact the correlation in the aromatic series is not linear for toluene and anisole.

These facts could be related to a different mechanism for the transfer reaction. Radical addition has been argued[2] in the case of the furan ring. On the other hand, the retarded radical polymerization of vinyl acetate using benzene as solvent is characterized by some features, all of which cannot be simultaneously explained by a conventional degradative transfer. Thus, donor–acceptor complex[10] or primary radical transfer[11] are leading alternatives.

In fact, the aromaticity of the furan ring is lower in comparison with the benzene ring[12], and its properties as a diene could be predominant in the case of radical attack.

Molecular-orbital calculations

In order to model the polymeric radical attack on the furan ring, the following dimer was used as the radical species with the aim to improve calculations with respect to the monomeric one previously reported[3]:

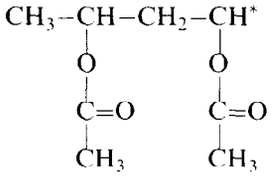

Table 3 Calculated energies for the HOMO, LUMO and SOMO for the radical attack on furan derivatives

Furan side group	Neutral molecules (eV)		Radicals formed (eV)	
	HOMO	LUMO	SOMO	LUMO
-CHO	−9.6	−0.4	−4.7	0.4
-$COCH_3$	−9.5	−0.3	−4.7	0.4
-$CONH_2$	−9.6	−0.3	−4.7	0.5
-COOH	−9.7	−0.4	−4.8	0.4
-CH_2NH_2	−9.1	0.6	−4.1	1.2
-CH_2OH	−9.1	0.5	−4.1	1.1
-H	−9.1	0.7	−4.1	1.1
-CH_3	−9.0	0.6	−4.1	1.1
Vinyl acetate	−9.7	0.5	−4.2	0.9

Table 4 Other calculated electronic and molecular properties

Side group	Ionization potential (eV)	Dipole moment (D)		Enthalpy of reaction (kJ mol^{-1})
		Neutral	Radical	
-CHO	9.58	2.80	4.22	0.39
-$COCH_3$	9.51	2.72	3.86	4.42
-$CONH_2$	9.60	3.32	4.22	−2.28
-COOH	9.67	2.22	4.57	7.75
-CH_2NH_2	9.07	0.90	2.53	−12.78
-CH_2OH	9.05	0.83	0.90	0.30
-H	9.14	0.42	2.09	2.64
-CH_3	9.03	0.40	2.10	1.43
Correlation coefficient	−0.91	−0.94	−0.88	−0.054

Radical addition was supposed to occur on the C5 of the furan ring, as was pointed out in the 'Introduction'.

The energies of the highest occupied, lowest unoccupied and singly occupied molecular orbitals (HOMO, LUMO and SOMO) for the attacking radicals, the neutral molecules and the radicals formed were calculated in the conformation of their respective minimum total energy according to their optimized geometries which have been reported and they are shown in *Table 3*.

A very interesting difference clearly occurs between the strongest retarders and the weakest ones, there being no significant differences among compounds in each group. This is due to the π nature of frontier orbitals, mainly localized in the ring without significant participation of substituents in spite of the possibilities of conjugation.

The first four neutral compounds have the lower energies of the HOMO and LUMO. Precisely, they are the strongest retarders. The interaction of the SOMO for the dimeric radical with these molecules must be through their respective LUMO. Furthermore, SOMO of radicals formed in these cases are the lowest in *Table 3*, indicating that the retardation is due to a greater stabilization of the SOMO for these radicals with respect to the attacking radical.

The last four furan compounds behave as weaker retarders. The interaction must be SOMO–HOMO as expected from *Table 3*. The energies of the SOMOs for their resulting radicals are similar to that of the attacking radical.

These results are in agreement with the scheme given by Saunders for alternating copolymerization[13]. However, these calculations could not give the differences in retarders among molecules of each group.

Other electronic and molecular properties were calculated and are shown in *Table 4*. The theoretical dipole moments of the radicals are greater than those of the molecules as expected for these species.

The approximate MNDO enthalpies of radical addition to the furan ring are very low or positive and do not correlate with the rate of polymerization from *Table 1*. The values of the enthalpy are essentially the same as already reported[3], but a monomeric radical was used as the attacking species in that case.

This could indicate that the accuracy of MNDO heat of formation is too poor for establishing such differences, but some series on MNDO calculations for furan compounds have previously agreed with the experimental tendencies[12]. On the other hand, the double bonds of the furan rings are strongly hindered because they are 1,2 and 1,2,3 substituted. This behaviour must be determined by a steric factor rather than a polar one as has been suggested by Tedder[14] to explain the low-enthalpy radical addition in the case of simple olefins.

The ionization potential in the case of the furans does not follow the pattern found by Benson[15] for radical addition to methyl-substituted ethylenes. According to the latter results the activation energy decreases as the ionization potential decreases because a polar factor must be controlling the rate. In our case the weaker retarders have lower ionization potentials. Thus, a polar factor cannot be determining the process.

Those facts pointed out that the retardation process is not thermochemically controlled due to steric hindrance.

However, the calculated dipole moments of the neutral molecules (*Table 4*) show a good correlation with the rate of polymerization (R_p) except for the furamide. Thus, the dipole moment is quite sensitive to detect the retarding power of these compounds. As a rule a greater dipole moment implies a greater possibility of stabilization for the radical to be formed. It is a clear indication that the capability of retardation is differentiated in the neutral reacting molecules mainly by a pure orbital factor, i.e. the influence of substituents in frontier orbitals.

CONCLUSIONS

Furan compounds display different retarding features over the radical polymerization in comparison with the benzene analogues. This suggests a particular mechanism of action. In this context the MNDO method has shown, in a more quantitative way than the qualitative frontier orbital analysis, that an interaction of the type SOMO–LUMO seems to determine the formation of the more stabilized radical leading to stronger degradative transfer processes. Calculated dipole moments of neutral molecules have a predictive power with respect to this retarding capacity.

REFERENCES

1 Gandini, A. and Rieumont, J. Preprints International Symposium on Free Radical Polymerization, Santa Margherita Ligure, Genoa, Italy, 1987, p. 73
2 Gandini, A. and Rieumont, J. *Tetrahedron Lett.* 1976, 2101
3 Paz, J. A., Vega, R., Rieumont, J., Montero, L. A. and Alvarez, J. R. *Makromol. Chem., Theor. Simul.* 1992, **1**, 99
4 Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.* 1977, **99**, 4899
5 Fletcher, R. and Powell, M. J. D. *Comput. J.* 1965, **6**, 163
6 Montero, L. M. and Alvarez, J. R. *Folia Chim. Theor. Latine* 1988, **XVI**, 33
7 Paz, J. A. and Rieumont, J. to be published
8 Jaffe, H. H. *Chem. Rev.* 1953, **53**, 191
9 Swain, G. C. and Lupton, C. *J. Am. Chem. Soc.* 1968, **90**, 4328
10 Kamachi, M. *Adv. Polym. Sci.* 1981, **38**, 55
11 Rieumont, J. *Acta Polym.* 1986, **37**, 422
12 Alvarez, J. R., Cuza, D., Montero, L. A. and Isoba, R. *J. Mol. Struct. (Theochem)* 1990, **209**, 361
13 Fleming, I. 'Frontier Orbitals and Organic Chemical Reactions', Wiley, London, 1976, p. 145
14 Tedder, J. M. *Angew. Chem., Int. Edn. Engl.* 1982, **21**, 401
15 Benson, S. W. 'Thermochemical Kinetics', Wiley, New York, 1976, p. 194
16 Lindemann, M. R. 'Vinyl Polymerization' (Ed. A. E. Ham), Marcel Dekker, New York, 1967, p. 207