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MOLECULAR ORBITAL THEORY PREDICTION OF PRIMARY FRAGMENTATION SITES IN TETRACYCLIC DITERPENOIDS

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Semiempirical molecular orbital calculations have been carried out for kaurene, phyllocladene, phyllocladane and 17-norphyllocladene. The differences in bond orders between the neutral molecule and the bication correlate rather well with the observed gross features of fragmentation in kaurene and phyllocladene, the differences in bond orders in the cation follow the same trend and allow prediction of many peaks for the previously undescribed mass spectra of 17-norphyllocladane and phyllocladane. Thus a primary mass spectra is obtained for these relatively complicated diterpene structures.

As a consequence of the line of investigation followed by our laboratory which has been centered on the study of the mass spectra of ^{13}C labelled hydrocarbons,[1] we became interested on the possibility of theoretically predicting the primary fragmentation in tetracyclic diterpenes. Since it has been shown that no extensive randomization is evident at the molecular ion level,[2] it seems that one can still discuss the fragmentation process in terms of some specially favorable fragmentations. Usually, fragmentation behavior is quite complex and is rationalized in terms of an empirical model of molecular dynamics, based on groundstate chemistry, including such concepts as radical, ion statility as well as electron donating and withdrawing character.

But it is desirable to place even qualitative features of mass spectra on firmer theoretical grounds. With this idea in mind the Quasiequilibrium theory of mass spectra was developed. This statistical approach is capable of prediction for relatively simple saturated hydrocarbons,[3,4] however it is not suitable for large systems, although some recent successful calculations are available.[5,6]

TABLE 1. BOND ORDERS CALCULATED BY CNDO/2 METHOD

Molecule	Phyllocladene			Kaurene		Phyllocladane			17-Norphyllocladane		
Bond	M°	M⁺	M⁺²	M°	M⁺²	M°	M⁺	M⁺ᵇ	M°	M⁺	M⁺²
1-2	1.019	0.988	0.959	1.019	0.935	1.019	0.988	0.959	1.019	0.988	0.959
1-10	0.981	0.891	0.844	0.979	0.870	0.981	0.893	0.844	0.981	0.891	0.841
2-3	1.030	1.040	1.053	1.029	1.049	1.030	1.039	1.053	1.030	1.040	1.054
3-4	0.976	0.945	0.916	0.976	0.945	0.976	0.946	0.914	0.976	0.944	0.910
4-5	0.959	0.866	0.766	0.957	0.759	0.959	0.868	0.758	0.959	0.865	0.762
5-6	1.006	0.957	0.935	1.007	0.973	1.006	0.959	0.943	1.006	0.956	0.930
5-10	0.968	1.065	1.072	0.972	1.040	0.968	1.002	1.053	1.005	1.003	1.057
6-7	1.027	0.985	0.944	1.033	0.953	1.027	0.966	0.946	1.027	0.966	0.945
7-8	1.003	1.026	1.057	0.980	1.012	1.004	1.028	1.058	1.004	1.026	1.058
8-9	0.953	0.826	0.754	0.978	0.900	0.954	0.825	0.757	0.954	0.828	0.760
8-14	0.983	0.935	0.878	0.977	0.803	0.984	0.936	0.884	0.965	0.939	0.887
8-15	0.974	0.975	0.976	0.978	0.976	0.970	0.969	0.967	0.969	0.969	0.967
9-10	0.973	0.865	0.778	0.968	0.756	0.973	0.866	0.784	0.973	0.866	0.782
9-11	1.016	1.020	1.049	1.007	0.959	1.016	1.029	1.048	1.016	1.020	1.048
11-12	1.021	0.909	0.963	1.017	0.973	1.022	0.999	0.865	1.022	1.000	0.966
12-13	0.987	0.988	0.991	0.994	1.003	1.000	0.999	1.001	1.000	0.997	0.998
13-14	0.995	0.998	1.004	0.988	0.979	1.001	1.004	1.010	1.000	1.003	1.009
13-16	0.983	0.879	0.971	0.997	0.966	0.972	0.967	0.990	0.992	0.988	0.981
15-16	1.009	1.006	1.002	1.000	0.997	0.969	0.997	0.991	1.020	1.018	1.016
16-17	1.939	1.947	1.947	1.943	1.950	1.021	1.018	1.012	-	-	-
4-17	-	-	-	-	-	-	-	-	1.010	1.014	1.015
4-18	-	-	-	-	-	-	-	-	1.001	1.004	1.009
10-19	-	-	-	-	-	-	-	-	1.003	1.010	1.015
4-18	1.010	1.014	1.018	1.011	1.014	1.010	1.014	1.018	-	-	-
4-19	1.001	1.004	1.008	1.006	1.007	1.001	1.004	1.009	-	-	-
10-20	1.003	1.010	1.016	1.004	1.012	1.003	1.010	1.016	-	-	-

TABLE 2. DIFFERENCES BETWEEN BOND ORDERS x 10³

Molecule	Phyllocladene		Kaurene	Phyllocladane		17-Norphyllocladane	
Bond	M°-M⁺	M⁺-M⁺²	M°-M⁺²	M°-M⁺	M⁺-M⁺²	M°-M⁺	M°-M⁺²
1-2	31	60	84	31	60	31	60
1-10	90	137	109	88	137	90	140
2-3	-10	-23	-20	-9	-23	-10	-24
3-4	31	60	32	33	62	32	66
4-5	93	191	198	91	201	94	197
5-6	49	71	34	47	72	50	76
5-10	-35	-87	-68	34	-85	-35	-89
6-7	43	83	80	41	81	41	82
7-8	-23	-54	-32	-24	-54	-24	-54
8-9	127	199	129	107	197	126	194
8-14	48	105	74	49	101	46	98
8-15	-1	-2	2	1	3	0	2
9-10	108	195	212	107	189	107	191
9-11	-13	-33	-48	-13	-32	-13	-32
11-12	22	58	44	23	57	22	56
12-13	-1	-4	-9	1	-1	1	0
13-14	-3	-9	7	-3	-9	-3	-9
13-16	4	12	11	5	13	4	11
15-16	3	7	3	2	8	2	4
16-17	-8	-8	-7	3	9	-	-
4-17	-	-	-	-	-	-4	-9
4-18	-	-	-	-	-	-3	-8
10-19	-	-	-	-	-	-7	-12
4-18	-4	-8	-3	-4	-8	-	-
4-19	-3	-7	-1	-3	-8	-	-
10-20	-7	-13	-8	-3	-8	-	-

These differences refer to bond orders in Table 1.
Underlined values correspond to those bonds which are appreciably weakened.
Negative values correspond to bonds which are strengthened.

The applications of quantum mechanical calculations have been done with somewhat greater success. Loew, Chadwick and Smith have carried out semiempirical molecular orbital calculations for the steroidal hormone estrone[7] and have established that, bond orders of the ground state and excited electronic state of the molecular ions provide a basis for distinction among sites of initial bond cleavage which might give information for subsecuent fragmentation of the molecular ion. An analogous approach has been followed by Yamamoto and Hirota.[8]

In this case we chose diterpenic hydrocarbons because there is enough information concerning its mass spectral fragmentation including that from ¹³C labelling experiments,[2] and low energy mass spectrometry. Moreover, they are comparatively simple as they do not have atoms with large differences in electronegativity, so hopefully the approximations used will affect them little and charge localization will be a relatively trivial problem.

TABLE 3. PRIMARY MASS SPECTRA

Phyllocladane			17-Norphyllocladane		
m/e	Formula	Probable Origin	m/e	Formula	Probable Origin
274	C₂₀H₃₄	M⁺	260	C₁₉H₃₂	M⁺
259ᵃ	C₁₉H₃₁	(M-15)⁺	245ᵃ	C₁₈H₂₉	(M-15)⁺
246	C₁₈H₃₀	(M-28)⁺	232	C₁₇H₂₈	(M-28)⁺
245	C₁₈H₂₉	(M-29)⁺	231	C₁₇H₂₇	(M-29)⁺
233	C₁₇H₂₉	(M-41)⁺	219	C₁₆H₂₇	(M-41)⁺
232	C₁₇H₂₈	(M-42)⁺	218	C₁₆H₂₆	(M-42)⁺
231	C₁₇H₂₇	(M-43)⁺	217	C₁₆H₂₅	(M-43)⁺
205	C₁₅H₂₅		191	C₁₄H₂₃	
204	C₁₅H₂₄		176	C₁₃H₂₀	
190	C₁₄H₂₂		175	C₁₃H₁₉	
189	C₁₄H₂₁		165	C₁₂H₂₁	
165	C₁₂H₂₁		164	C₁₂H₂₀	
164	C₁₂H₂₀		150	C₁₁H₁₈	
150	C₁₁H₁₈		149	C₁₁H₁₇	
149	C₁₁H₁₇		148	C₁₁H₁₆	
148	C₁₁H₁₆		147	C₁₁H₁₅	
147	C₁₁H₁₅		138	C₁₀H₁₇	
138	C₁₀H₁₈		137	C₁₀H₁₆	
137	C₁₀H₁₇		136	C₁₀H₁₅	
136	C₁₀H₁₆		135	C₁₀H₁₅	
135	C₁₀H₁₅		124	C₉H₁₆	
124	C₉H₁₆		123	C₉H₁₅	
123	C₉H₁₅		122	C₉H₁₄	
122	C₉H₁₄		109	C₈H₁₃	
109	C₈H₁₃		108	C₈H₁₁	
108	C₈H₁₂		95	C₇H₁₁	
			94	C₇H₁₀	

ᵃ Not Predicted Theoretically
ᵇ Fragments with less than 7 carbon atoms are not included
Fragments included here correspond with two and three bonds ruptures with large added bond order differences (Table 2)

TABLE 4. EXPERIMENTAL MASS SPECTRA*

	% Relative Intensity	
m/e	Kaurene	Phyllocladene
257	40	17
244	5	3
243	4	3
230	29	8
229	85	22
216	8	3
203	10	3
201	11	3
189	13	4
187	39	10
178	3	1
175	22	8
165	2	1
161	17	5
159	19	9
152	--	1
151	3	3
148	38	12
138	6	1
133	32	16
124	20	7
121	27	12
120	38	14
111	10	5
107	41	22
93	44	33

* Ref. 16

METHODS AND CALCULATIONS

Our quantum mechanical calculations are based on semi-empirical methods, CNDO/2[9],[10] and PCILO.[11] We found that there is a close relations between the differences in bond orders[12] comparing the neutral molecule with the cation or bication and the initial fragmentation trends observed in a mass spectrometer.

Determination of the Conformations

The molecular conformations of the compounds under study, phyllocladene 1, kaurene 2, phyllocladane 3, and 17-norphyllocladane 4, were derived from crystallographic data for analogous molecules and further optimization of the geometric parameters in terms of the total

Fig. 1 Bond length and Angles in Phyllocladene

energy in the molecular system by means of the PCILO method.[13] In this context, the geometry for 17-norphyllocladane (4), was derived from X-ray data for Beyeran-3-α-ol p-bromo benzene sulphonate[14] (without the methyl group at C₁₃); that for phyllocladane (3) was obtained by insertion of a methyl group at C₁₃ and optimization of its conformation. The geometry for phyllocladane (2) was found by inclusion of a double bond to 3

Fig. 2 Bond Length and Angeles in Kaurene

(C₁₆-C₁₇) and modification of the parameters for rings C and D to an optimal value for energy. Fianlly kaurene (4) geometry was obtained by the combination of crystallographic data for rings A and B in Beyeran-3α-ol p-Bromo benzene sulphonate (only distances and angles) and those for rings C and D from 7-OH Kaurenolide[14] and subsequent calculation of optimal values for bond angles C₇-C₁₀-C₉ and C₁₀-C₉-C₁₁ as well as for dihedral angles C₆-C₇-C₈-C₁₄ and C₇-C₈-C₁₅-C₁₆.

Fig. 3 Bond Length and Angles in Phyllocladene

The resulting geometric parameters were used in a CNDO/2 program in order to evaluate the electronic densities and Wiberg bond orders[15] for the neutral molecules, their cations (except in the case of kaurene on account of excessive computing time) and bications for the compounds under study.

Fig. 4 Bond Length and Angles in 17-Norphyllocladane

RESULTS AND DISCUSSION

Values for electronic densities at the atomic centers, for compounds 1, 2, 3 and 4 do not seem

to correlate with fragmentation patterns in any direct way in consonance with earlier reports.[7] On the other hand, bond orders (Table 1) and specially the differences between these values for the neutral molecule M^o, cation M^+ (when available), and bication M^{+2} (Table 2) does seem to correlate rather nicely with initial fragmentation pathways. Considering that most fragmentation require the rupture of at least two bonds the most probable fragmentations will be those showing the largest bond weakening for the bonds involved. This bond weakening is related to the differences in bond orders between the neutral molecule and the cation although those for the bication are even more pronounced and follow the same trend with the advantage that they consume less computing time. Thus as illustrated in scheme 1 there are a certain number of theoretically most favorable ruptures indicated as a_1, a_2, a_3, a_4, a_5 (ring A), and b_1, b_2, b_3, b_4 (ring
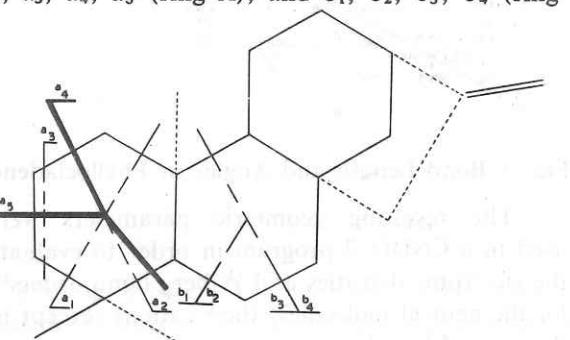
Scheme I Most favorable ruptures in Phyllocladene

B). To those fragmentations it is possible to add some three bond ruptures including rings B and C as well as C and D, in scheme 1 which could also make a certain contribution. Our results are in good agreement with those obtained for ^{13}C labelled kaurene and phyllocladene.[16] Using this approach it is possible to obtain a primary mass spectrum for 17-norphyllocladane and phyllocladane (Table 3). It seemed locical to include some simple rearrangements known to form stable fragments as the loss of one hydrogen from each fragment (hydrogen transfer) and to include empirically the M-15 fragment which although not predicted, at this first stage is always present in this type of compounds. The spectra considers equel possibility for charge location at both pieces of a certain fragment. These theoretical primary fragmentation is of an entirely predictive nature since the mass spectra of compounds 3 and 4

have not been described or carried our previously. One would expect a better correlation for low energy mass spectra, since they will have less fragments corresponding to rearrangements and a greater sellectivity for bond rupture and this is apparently the case for kaurene at 14 eV.[1] Of course it is still not possible to include relative intensities of these fragments, in this static approach to the problem since they would depend both on the speed of formation and the speed of decomposition and we do not have enough information about the relative stability of each fragment. Moreover, quite frequently they have multiple origins as has been pointed out previously. Nevertheless we know from metaestable ion information that most of them arise directly from the molecular ion at least to a large extent and it is this part of the mass spectra which correspond to the initial fragmentation.[1]

CONCLUSION

Using semiempirical Quantum mechanical calculations it is possible to predict primary fragmentation pathways for the relatively complicated molecules 17-norphyllocladane and phyllocladane, spite of our supposition that bonds are broken in the intact molecular ion, i.e., that no isomers of the molecular ion form as intermediates. The method has given good correlation for the isomeric diterpene molecules phyllocladene and kaurene for which there is experimental information including ^{13}C labelling and low energy mass spectra (Table 4).[16] In general there is better agreement for low energy mass spectra. The inclusion of some empiric common rearrangements allow the prediction of most fragments originating from the molecular ion and constitute a theoretical primary mass spectra.

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ESTUDIO CINETICO DE LA ADSORCION DE ACIDOS ORGANICOS EN SOLUCION ACUOSA SOBRE CARBON ACTIVADO I

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RESUMEN. Se ha seguido potenciométricamente la velocidad de adsorción del ácido acético en solución acuosa sobre el carbón activado de origen vegetal. La curva pH — Tiempo que se obtiene indica que la adsorción sigue un modelo cinético de 1er. orden respecto a cada reactivo. Se obtuvo las constantes de velocidad de adsorción a cuatro temperaturas y se aplicó la ecuación de Arrhenius.

ABSTRACT. The adsorption rate of acetic acid from aqueous solution on activated carbon has been measured by potentiografic method. The pH — time graph analysis gives a first order kinetic model for each reactive (carbon and acid). We   obtain the rate constant values at four temperatures and activation parameters through the Arrhenius equation.

INTRODUCCION

La adsorción de ácidos orgánicos ha sido investigada desde hace mucho tiempo[1] desde el punto de vista del equilibrio:

$$Ac.\ Org.\ +\ Superficie \rightleftharpoons Sorbato \qquad (1)$$

tanto teórica como experimentalmente. Las isotemas de adsorción de los ácidos carboxílicos se utilizan comúnmente para la determinación de superficies en carbones activados[2]. Sin embargo nos parece que se ha estudiado poco las cinéticas de adsorción o desorción[3], las direcciones que implica el equilibrio en la reacción 1. En este trabajo proponemos el método potenciométrico para obtener las velocidades de adsorción de los ácidos orgánicos en solución acuosa.

Método Potenciográfico. Este método consiste en obtener una curva que da el pH como función del tiempo. Se ha usado un Potenciógrafo Metrohm E 436 dotado de un electrodo combinado EA 121 UX y vasijas de titulación de 50 ml encamisadas para mantener la temperatura constante. Fué utilizado carbón vegetal activado marca Sigma después de lavarlo hasta su neutralización.

La técnica experimental fué la siguiente: 50

ml de solución ácida (aprox. M/250) a la temperatura del baño se colocan en la vasija de titulación, con agitación magnética y se espera que la temperatura se haga constante. En un pesafiltros de 30 ml se pesó previamente cierta cantidad de carbón. El peso total (pesafiltro + carbón) lo llamamos w_i. Cuando la temperatura de la vasija de titulación se ha estabilizado, se adiciona al pesafiltro 15 ml de agua, a la temperatura del baño y se introduce al baño unos minutos para reestabilizar su temperatura. En este tiempo se conecta el potenciógrafo y, cuando se ha estabilizado la señal pH, se hace funcionar el registrador (que ahora marca un pH constante). Cuando se ha hecho lo anterior, se agita el pesafiltros con su contenido, se destapa y se vierte rápidamente la dispersión contenida a la solución que estaba en el vaso de titulación. El pesafiltros se seca y pesa de nuevo para obtener el peso W_c del carbón adicionado.

La Curva pH - tiempo

La figura 1 representa un trazo del registrador de la curva pH ante tiempo, antes y después de la adición de la dispersión del carbón. A partir del instante de la adición se observan 3 zonas en la curva. a) una porción inmediata a la adición del adsorbente que muestra que el pH aumenta (la solución tiende a la neutralidad) al transcurrir el tiempo. b) Una porción curva en la que se observa que el pH cambia poco respecto al tiempo. c) Una porción de hecho paralela al eje del tiempo, en la que el pH casi no varía.