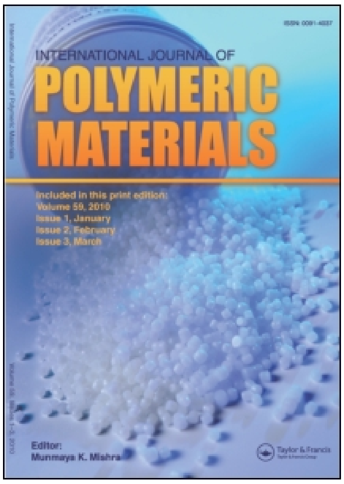

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Theoretical Estimation of Acid Strength of Boron-Fluoride-Alcohol Complexes during Cationic Polymerization of Olefins

K. S. Minsker[a]; V. A. Babkin[a]; G. E. Zaikov[b]
[a] Bashkirian State University, ufa, Russia [b] Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

To cite this Article Minsker, K. S. , Babkin, V. A. and Zaikov, G. E.(1995) 'Theoretical Estimation of Acid Strength of Boron-Fluoride-Alcohol Complexes during Cationic Polymerization of Olefins', International Journal of Polymeric Materials, 28: 1, 77 — 81

To link to this Article: DOI: 10.1080/00914039508012089

URL: http://dx.doi.org/10.1080/00914039508012089

Intern. J. Polymeric Mater., 1995, Vol. 28, pp. 77–81
Reprints available directly from the publisher
Photocopying permitted by license only

Theoretical Estimation of Acid Strength of Boron-Fluoride-Alcohol Complexes during Cationic Polymerization of Olefins

K. S. MINSKER and V. A. BABKIN

Bashkirian State University, Frunze Str. 4, ufa, 450071, Russia

and

G. E. ZAIKOV

Institute of Chemical Physics, Russian Academy of Sciences, Kosygin Str. 4, Moscow 117334, Russia

(Received July 10, 1994)

The quantum-chemical investigations of ROH·$BRnF_3$-*n*-complexes were carried out and their acidic strength determine as function of alcohols and ligand characteristics and the environment of the heteroatom B.

KEY WORDS Alcohol boron fluoride complexes, acidic strength, quantum chemical calculations, cationic polymerization, olefins.

INTRODUCTION

Complexes of alcohols (CH_3OH, C_2H_5-OH, Izo-C_3H_7, t-C_4H_9) and boron fluoride $BRnF_3$-*n* (here $n = 0, 1, 2, 3$; $R = CH_3$, C_2H_5, izo-C_3H_7, t-C_4H_9) are the traditional acidic catalysts of polymerization of olefins.[1-3] Change of the nature of proton donors-alcohols and of ligand environment of B provides the formation of initiating systems with wide range of activity.

The labile character of these systems is indicated by the changes in their nature and composition during storage or in the reacting medium. Hence, it is difficult to carry out the analysis of their catalytic and acidic properties. One of the important features which determine catalytic properties of ROH·$BRnF_3$-*n* is the acidic strength on which their activity in various processes depends. As there are no reliable methods for experimental determination of acidic strength (pKa) of H-complexes,[2] the theoretical methods of estimating such characteristics of these systems as the charge on H-atom ROH-q_{H+}, plays an important role, because this charge correlates with the universal exponent of acidity pKa.[4]

Dependence of the electrophilic activity of alcohols in complexes on the acidic strength and the resulting possibility of demonstrating both protonodonor and carbocationic activities under the influence of Lewis and Brönsted acids allow us to establish, on the basis of theoretical quantum-chemical calculations, the correlation between acidic and catalytic properties of boron fluoride-alcohol complexes.

The quantum-chemical calculations of ROH·$BRnF_3$-*n*-complexes have not been done, their acidic strength was not estimated, and its influence on the catalytic activity has not yet been studied.

Therefore, we carried out the quantum-chemical investigation of ROH·$BRnF_3$-*n*-complexes and determined their acidic strength dependence on the nature of alcohols and ligand environment of the heteroatom B. The data are analysed and systematized.

MODELS AND PROCEDURE OF CALCULATIONS

Quantum-chemical calculations of ROH·$BRnF_3$-*n*-complexes were done by CNDO/2 method in classic parametrization of Santry-Pople-Segal.[5,6] The optimization of geometry of the complexes under study was done by changing matrices.[7] The structure of complexes for all models was assumed to be tetrahedronal, according to minimum energy of the main system state. The values of initial lengths and angles between them were taken from Reference 7.

The calculation was done in approximation of the isolated molecule in the gas phase. The parameters of acidic strength of complexes were represented by the charges of H^+ atoms of ROH-alcohols and the values of the universal exponent of acidity pKa. Bond order for the alcohols in the complexes with boron fluoride P_{OH} and P_{OC} in the estimation of the influence of acidic strength on manifestation by alcohols of proton-donor/carbocationic activity were determined according to Armstrong.[8]

RESULTS OF CALCULATIONS AND THEIR DISCUSSION

Table I gives the parameters of acidic strength (q_{H_+} and pKa), bond orders P_{OH} and P_{OC}, and corresponding activities-H^+ (protodonor) or R^+ (carbocationic) of alcohols in ROH·$BRnF_3$-*n* systems.

If both H^+ and R^+ stand in one column of the table, then it means that carbocationic and protonodonor activities of alcohols are equally possible. For easy comparison of results of calculations all 52 model compounds under study are subdivided into 13 groups which differ from each other by the nature of ligand environment of boron. Electronic structure and geometry of boron fluoride-alcohol models after geometry optimization by alternative metric method represent distorted tetrahedronal configurations similar in their characteristics to those represented in work.[7] (Bond length of R_{OH} = 0.11 nm, R_{BF} = 0.135 nm, R_{OB} = (0.17 ± 0.005) nm, R_{OH} = 0.109 nm, R_{CC} = (0.132 ± 0.004) nm. Angles between ligands B = 109 ± 18°, angles of alcohol HOR = 114 ± 10°). All the models

TABLE I

Parameters of acidic strength and bond orders P_{OH} and P_{OC} of the complexes $RnBF_{3-n} \cdot ROH$

N *n/n*	Model	q_{H^+} ($\pm$0.02)	pKa	P_{OH}	P_{OC}	Activity	N group
1	$F_3B \cdot OHCH_3$	+0.24	+1.0	0.92	0.98	H^+	I
2	$F_3B \cdot OHC_2H_5$	+0.23	+1.5	0.92	0.97	H^+	
3	$F_3B \cdot OHC_3H_7$	+0.21	+7.1	0.92	0.94	H^+, R^+	
4	$F_3B \cdot OHC_4H_9$	+0.20	+7.3	0.93	0.90	R^+	
5	$F_2CH_3B \cdot OHCH_3$	+0.23	+1.5	0.92	1.01	H^+	II
6	$F_2CH_3B \cdot OHC_2H_5$	+0.22	+4.4	0.92	0.96	H^+	
7	$F_2CH_3B \cdot OHC_3H_7$	+0.20	+7.3	0.93	0.90	R^+	
8	$F_2CH_3B \cdot OHC_4H_9$	+0.19	+7.7	0.93	0.89	R^+	
9	$F(CH_3)_2B \cdot OHCH_3$	+0.23	+1.5	0.92	1.00	H^+	III
10	$F(CH_3)_2B \cdot OHC_2H_5$	+0.21	+7.1	0.94	0.97	H^+	
11	$F(CH_3)_2B \cdot OHC_3H_7$	+0.20	+7.3	0.92	0.94	H^+, R^+	
12	$F(CH_3)_2B \cdot OHC_4H_9$	+0.20	+7.3	0.93	0.90	R^+	
13	$(CH_3)_3B \cdot OHCH_3$	+0.24	+1.0	0.94	0.96	H^+, R^+	IV
14	$(CH_3)_3B \cdot OHC_2H_5$	+0.23	+1.5	0.92	0.95	H^+	
15	$(CH_3)_3B \cdot OHC_3H_7$	+0.22	+4.4	0.91	0.91	R^+	
16	$(CH_3)_3B \cdot OHC_4H_9$	+0.20	+7.3	0.89	0.89	R^+	
17	$F_2C_2H_5B \cdot OHCH_3$	+0.23	+1.5	0.93	0.98	H^+	V
18	$F_2C_2H_5B \cdot OHC_2H_5$	+0.22	+4.4	0.92	0.96	H^+	
19	$F_2C_2H_5B \cdot OHC_3H_7$	+0.22	+4.4	0.94	0.93	H^+, R^+	
20	$F_2C_2H_5B \cdot OHC_4H_9$	+0.21	+7.1	0.93	0.89	R^+	
21	$F(C_2H_5)_2B \cdot OHCH_3$	+0.24	+1.0	0.92	0.97	H^+	VI
22	$F(C_2H_5)_2B \cdot OHC_2H_5$	+0.23	+1.5	0.92	0.95	H^+	
23	$F(C_2H_5)_2B \cdot OHC_3H_7$	+0.21	+7.1	0.92	0.93	H^+, R^+	
24	$F(C_2H_5)_2B \cdot OHC_4H_9$	+0.20	+7.3	0.93	0.90	R^+	
25	$(C_2H_5)_3B \cdot OHCH_3$	+0.22	+4.4	0.92	0.90	H^+	VII
26	$(C_2H_5)_3B \cdot OHC_2H_5$	+0.21	+7.1	0.93	0.95	H^+, R^+	
27	$(C_2H_5)_3B \cdot OHC_3H_7$	+0.21	+7.1	0.92	0.93	H^+, R^+	
28	$(C_2H_5)_3B \cdot OHC_4H_9$	+0.20	+7.3	0.93	0.90	R^+	
29	$F_2C_3H_7B \cdot OHCH_3$	+0.23	+1.5	0.92	0.98	H^+	VIII
30	$F_2C_3H_7B \cdot OHC_2H_5$	+0.22	+4.4	0.93	0.97	H^+, R^+	
31	$F_2C_3H_7B \cdot OHC_3H_7$	+0.20	+7.3	0.92	0.93	H^+, R^+	
32	$F_2C_3H_7B \cdot OHC_4H_9$	+0.20	+7.3	0.92	0.89	R^+	
33	$F(C_3H_7)_2B \cdot OHCH_3$	+0.24	+1.0	0.92	0.99	H^+	IX
34	$F(C_3H_7)_2B \cdot OHC_2H_5$	+0.24	+1.0	0.93	0.96	H^+	
35	$F(C_3H_7)_2B \cdot OHC_3H_7$	+0.21	+7.1	0.93	0.94	H^+, R^+	
36	$F(C_3H_7)_2B \cdot OHC_4H_9$	+0.20	+7.3	0.92	0.89	R^+	
37	$(C_3H_7)_3B \cdot OHCH_3$	+0.22	+4.4	0.92	0.99	H^+	X
38	$(C_3H_7)_3B \cdot OHC_2H_5$	+0.22	+4.4	0.92	0.96	H^+	
39	$(C_3H_7)_3B \cdot OHC_3H_7$	+0.21	+7.1	0.92	0.93	H^+, R^+	
40	$(C_3H_7)_3B \cdot OHC_4H_9$	+0.19	+7.7	0.92	0.89	R^+	
41	$F_2(C_4H_9)B \cdot OHCH_3$	+0.23	+1.5	0.92	0.99	H^+	XI
42	$F_2C_4H_9B \cdot OHC_2H_5$	+0.21	+7.1	0.93	0.96	H^+	
43	$F_2C_4H_9B \cdot OHC_3H_7$	+0.21	+7.1	0.92	0.93	H^+, R^+	
44	$F_2C_4H_9B \cdot OHC_4H_9$	+0.20	+7.3	0.93	0.89	R^+	
45	$F(C_4H_9)_2B \cdot OHCH_3$	+0.23	+1.5	0.92	1.00	H^+	XII
46	$F(C_4H_9)_2B \cdot OHC_2H_5$	+0.22	+4.4	0.93	0.97	H^+	
47	$F(C_4H_9)_2B \cdot OHC_3H_7$	+0.22	+4.4	0.93	0.94	H^+, R^+	
48	$F(C_4H_9)_2B \cdot OHC_4H_9$	+0.19	+7.7	0.93	0.90	R^+	
49	$(C_4H_9)_3B \cdot OHCH_3$	+0.22	+4.4	0.93	1.00	H^+	XIII
50	$(C_4H_9)_3B \cdot OHC_2H_5$	+0.21	+7.1	0.93	0.96	H^+	
51	$(C_4H_9)_3B \cdot OHC_3H_7$	+0.20	+7.3	0.93	0.93	H^+, R^+	
52	$(C_4H_9)_3B \cdot OHC_4H_9$	+0.19	+7.7	0.93	0.91	H^+, R^+	

ROH·BRnF$_3$-*n* represent donor-acceptor complexes. Quantum-chemical proof of the fact is high negative values of the total energy of the systems (Ec = 302590–370990 kg/mol.) characterizing the stability of complexes. The part of the charge of electron transmitted to the receptor was equal to 0.07–0.09.

Transition of unbound electrons of oxygen ROH is performed by cRc-orbits to vacant Sp^2 orbits B^{3+}.

One can see from the table that the charge of hydrogen atom-q_{H+} of alcohols in complexes with BRnF$_3$-*n* decreases from 0.24 to 0.19 on branching of alcohol radicals in all 13 groups. It means that the charge q_{H+} does not depend on the nature of ligand environment of B and is determined by the nature of the alcohol radical R.

The acidic strength of complexes in accordance with correlative relation q_{H+} = pKa^4 decreases from 0.5–1.5 to 7.3–7.7 in the row of alcohols from CH_3OH to C_4H_9OH in fluoride boron complexes.

Bond order for all studied groups of complexes ROH·BRnF$_3$-*n* is practically unchanged and equals 0.94–0.92 (possible mistake of CNDO/2 method at the estimation of order of connections is approximately 0.02). The P_{OC} bond order decreases simultaneously with the reduction of the acidic strength. The comparison of bond orders of P_{OH} and P_{OC} shows that for CH_3OH and C_2H_5OH in complexes with boron fluoride the protonodonor activity is characteristic, and R$^+$ is characteristic of t-butyl one. In izopropyl alcohol both H$^+$ and R$^+$ activities are equally probable.

Two alternatives of the alcohol molecule fragmentation depending on the nature of the radical are experimentally proven for ROH·BF$_3$ complexes.[3] The quantum-chemical calculation shows that the analogical possibilities of ROH fragmentation are characteristic of complexes with boron-organic compounds BRnF$_3$-*n*. Moreover, for the models of ROH·BRnF$_3$-*n* type, where the nature of radical ligand environment of B coincides with the nature of alcohol radicals, i.e. for complexes $(CH_3)3B \cdot OHCH_3$, $(C_2H_5)3B \cdot OHC_2H_5$, $(C_3H_7)3B \cdot OHC_3H_7$, $(C_4H_9)3B \cdot OHC_4H_9$ the equal probability of developing H$^+$ and R$^+$ activities is noted.

One of the reasons explaining this result is the coincidence of groups of symmetry of the alcohol radical and of heteroatom B, leading to equalization of bond orders P_{OH} and P_{OC}. However, this hypothesis requires experimental verification.

Thus, according to the data of quantum-chemical calculations the ROH·BRnF$_3$-*n* complexes have low Brönsted acidity ($+0.5 \leq$ pKa $\leq +7.7$) and do not depend on the nature of ligand environment B. To some degree, the demonstration by alcohols in complexes of protonodonor and carbocationic activities in the reaction of polymerization is explained by the nature of alcohol radical. In the final analysis, the low acidic strength of complexes supposes the relation between acidic-catalytic properties of ROH·BRnF$_3$-*n* and the interaction with substrate.

References

1. J. Kennedy, "Cationic Polymerization of Olefins: A Critical Inventory," New York, 420 pp. (1975).
2. C. A. Alah, "Friedel-Crafts Chemistry," New York, 581 pp. (1973).
3. F. C. Dainton and C. B. B. M., Sutherland, *J. Polon Sci.*, **4**, 37–43 (1949).

4. W. Grabowski, M. Misono and Y. Yoneda, **61,** 103–108 (1980).
5. J. A. Pople and D. Z. Beveridge, "Approximate Molecule Original Theory," N.Y.: McGraw-Hill Book, p. 44 (1970).
6. P. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47,** 158–174 (1967).
7. U. E. Ezner and B. L. Erusalimski, "Electronical Aspect of the Reaction Polymerization," L.: Science, 180 p. (1976).
8. D. R. Armstrong, P. S. Perkins and J. J. P. Stewart, *J. Chem. Soc. Dolton Trans.*, 838–840 (1973).