8418 *J. Phys. Chem. A* **2000,** *104,* 8418−8423

Is There a Minimum Polarizability Principle in Chemical Reactions?

Uwe Hohm[†]

Institut für Physikalische und Theoretische Chemie der Technischen Universität Braunschweig,
Hans-Sommer-Strasse 10, D-38106 Braunschweig, F.R.G.

Received: April 13, 2000; In Final Form: June 15, 2000

For complete fragmentations of the type $A_mB_n... \rightarrow mA + nB + ...$ the change of the dipole polarizabilty $\Delta\alpha \equiv \sum_i \nu_i \alpha_i$ and its cube-root $\Delta\alpha_{CR} \equiv \sum_i \nu_i \alpha_i^{1/3}$ as well as the atomization energy D^{at} are calculated from literature data (ν_i is the stoichiometric coefficient). We have taken into account a large number of molecules containing the atoms H, C, N, O, S, P, F, Cl, Br, and I as well as the metals Fe and Os. The ranges of D^{at} and $\sum_i \nu_i \alpha_i$ covered by the fragmentations are between 150 and 15 000 kJ mol^{-1} and −6 and 170 × 10^{-41} C^2 m^2 J^{-1}, respectively. In most cases $\Delta\alpha > 0$ is observed, whereas we always find $\Delta\alpha_{CR} > 0$. Additionally, we observe a linear relationship $D^{at} = A_\mu + B_\mu \sum_i \nu_i \alpha_i^\mu$ between the atomization energy D^{at} and the sum of the dipole-polarizabilities of all chemical species taking part in the fragmentation. The linear relation is obtained for $\mu = 1$ and $^1/_3$. Our observation implies that the most stable isomer has the lowest polarizability and that in chemical reactions the most stable species (reactants or products) have the lowest sum of $\alpha^{1/3}$.

1. Introduction

During the last years extensive studies have been performed on the electronegativity χ, hardness η, softness S, and polarizability α of time-dependent systems.[1−4] These studies include chemical reactions as well as intramolecular vibrations and rotations.[1,4−6] From detailed theoretical studies it has been found that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible" (maximum hardness principle, MHP).[4,7,8] It was also stated that "the natural direction of evolution of any system is toward a state of mimimum polarizability" (minimum polarizability principle, MPP).[2] The latter principle can be thought of as a consequence of the inverse relationship between α and η and the validity of the maximum hardness principle.[3] Gázquez[9] has studied exchange reactions. He found that exchange reactions almost always go in the direction that produces the hardest molecule or the products of highest average hardness. A similar observation was made by Ghanty and Ghosh.[5] They observed that exchange reactions go in the direction of the smallest sum of cube-roots $\alpha^{1/3}$ of the polarizability. $\alpha^{1/3}$ is found to be proportional to the inverse hardness $1/\eta$ of an atom.[10]

In this paper we will concentrate on the dipole-polarizability α. If the minimum polarizability principle holds true there must be an interrelationship between the change of the polarizability α which occurs during the course of a chemical reaction and its thermochemistry. First we concentrate on the complete fragmentation (atomization) of molecules of the type $A_mB_n... \rightarrow mA + nB + ...$ For this reaction the atomization energy D^{at} can be calculated via

$$D^{at} = \sum_i \nu_i \Delta_f H_i^0 \qquad (1)$$

where $\Delta_f H_i^0$ is the standard enthalpy of formation of the reactant and the products (atoms). ν_i being the stoichiometric coefficient, which is negative for the reactants. The corresponding change in the polarizability α is

$$\Delta\alpha \equiv \sum_i \nu_i \alpha_i \qquad (2)$$

whereas the change in the cube-root (CR) of the polarizability is obtained via

$$\Delta\alpha_{CR} \equiv \sum_i \nu_i \alpha_i^{1/3} \qquad (3)$$

As already noted by Ghanty and Ghosh[5] the change of $\alpha^{1/3}$ sometimes is a more suitable indicator of the stability of a chemical system than the hardness η itself. We will, therefore, use this term in our further considerations.

2. Evaluation of Input Data

The standard enthalpies of formation $\Delta_f H^0$ are usually known with acceptable accuray. They can be found in standard data collections, e.g., the *Handbook of Chemistry and Physics*.[11] In the case of the dipole-polarizability α, however, one has to be much more careful. There are a number of very valuable collections of α (see, e.g., refs 11 and 12). But the refinement of experimental and theoretical techniques has shown that many of the values given in the literature are less accurate than suggested by the experimental or theoretical uncertainty.[13] Additionally, calculations of α with "black-box" methods still are not capable for producing polarizabilities with accuracies of 1.0% or better. Therefore, we have concentrated only on 108 molecules for which the dipole-polarizability seems to be known with acceptable accuracy. Additionally we have used the most recent available polarizabilities of the atoms H, C, N, O, P, S, F, Cl, Br, I, Li, Na, K, Rb, Cs, Fe, and Os; in particular, $\alpha(H) = 7.419$,[14] $\alpha(C) = 19.24$,[15] $\alpha(N) = 11.97$,[15] $\alpha(O) = 8.64$,[15] $\alpha(P) = 41.58$,[16] $\alpha(S) = 32.32$,[17] $\alpha(F) = 6.10$,[15] $\alpha(Cl) = 24.25$,[17] $\alpha(Br) = 33.91$,[17] $\alpha(I) = 55.07$,[18] $\alpha(Fe) = 93.98$,[17] $\alpha(Os) = 94.58$,[11] $\alpha(Li) = 244.8$,[19] $\alpha(Na) = 268.3$,[20] $\alpha(K) = 502.9$,[21] $\alpha(Rb) = 600.8$,[22] and $\alpha(Cs) = 704.3$[21] (all in 10^{-41} C^2 m^2 J^{-1}).

[†] E-mail: u.hohm@tu-bs.de. Fax (+49)(0)531−3914577.

10.1021/jp0014061 CCC: $19.00

TABLE 1: Dipole Polarizability α, Change of Dipole Polarizability Δα and $\Delta\alpha_{CR}$, and Atomization Energy D^{at} of Nonconjugated Compounds

molecule	$10^{41}\alpha$/C^2 m^2 J^{-1}	$10^{41}\Delta\alpha$/C^2 m^2 J^{-1}	$10^{41}\Delta\alpha_{CR}$/(C^2 m^2 J^{-1})$^{1/3}$	D^{at}/kJ mol^{-1}
iodine (I_2)	116.0[33]	−5.86	5.89	153
fluorine (F_2)	13.99[37]	−1.79	2.68	158
bromine (Br_2)	74.03[26]	−6.21	4.90	193
chlorine (Cl_2)	50.17[32]	−1.66	4.53	243
hydrogen chloride (HCl)	28.67[42]	3.00	3.84	432
hydrogen (H_2)	8.95[34]	5.89	3.93	436
oxygen (O_2)	17.46[34]	−0.18	3.25	497
nitrous oxide (NO)	18.99[34]	1.62	3.60	631
hydrogen sulfide (H_2S)	40.13[44]	7.03	7.89	726
water (H_2O)	15.90[34]	7.58	7.41	918
nitrogen (N_2)	19.36[34]	4.58	4.07	945
phosphine (PH_3)	53.85[11]	9.99	11.93	980
cyanogen iodide (ICN)	79.14[39]	7.14	9.65	1059
hydrogen peroxide (H_2O_2)	24.65[38]	7.47	10.98	1068
carbon monoxide (CO)	21.57[24]	6.31	4.20	1077
ammonia (NH_3)	24.01[34]	10.22	11.32	1162
cyanogen chloride (ClCN)	50.78[39]	4.69	8.96	1176
cyanogen bromide (BrCN)	59.79[39]	5.33	9.25	1122
phosphorus (P_4)	151.21[16]	15.12	18.38	1189
cyanogen fluoride (FCN)	30.52[39]	6.79	7.91	1224
hydrogen cyanide (HCN)	27.60[40]	11.03	8.39	1272
formic acid (HCOOH)	36.94[12,a]	14.42	15.84	1505
carbon dioxide (CO_2)	28.87[30]	7.65	8.01	1609
hydrazine (N_2H_4)	38.50[12,a]	15.12	19.39	1632
ethine (C_2H_2)	37.86[41]	15.46	12.72	1642
methane (CH_4)	28.45[31]	20.47	16.00	1665
methyl fluoride (CH_3F)	33.05[11]	14.55	15.40	1677
bromotrifluoromethane ($CBrF_3$)	62.47[43]	8.98	16.01	1715
formaldehyde (H_2CO)	27.26[12,a]	15.46	12.11	1728
trifluoromethane (CHF_3)	32.38[12,a]	12.58	14.92	1868
tetrafluoromethane (CF_4)	32.49[12,a]	11.15	14.64	1968
sulfur hexafluoride (SF_6)	49.53[30]	19.39	22.57	1971
trichlorethylene ($CHClCCl_2$)	111.60[12,a]	7.06	24.08	2023
methanol (CH_3OH)	35.94[12,d]	21.62	19.89	2039
1,1-dichloroethylene (Cl_2CCH_2)	87.12[12,a]	14.71	22.87	2115
ethene (C_2H_4)	45.82[31]	22.34	20.65	2253
acetonitrile (H_3CCN)	49.85[12,a]	22.86	21.15	2496
ethylene oxide (C_2H_4O)	49.29[12,a]	27.51	24.87	2607
acetaldehyde (H_3CCHO)	51.07[12,a]	25.73	24.78	2721
ethyl chloride (C_2H_5Cl)	71.21[12,a]	28.62	29.86	2757
ethane (C_2H_6)	48.74[31]	34.26	28.89	2818
dimethyl sulfide ($(CH_3)_2S$)	83.78[12,a]	31.54	34.19	3056
ethanethiol (C_2H_5SH)	82.11[12,a]	33.20	34.26	3064
dimethyl ether ($(CH_3)_2O$)	57.41[12,a]	34.23	32.87	3175
ethanol (C_2H_5OH)	56.41[12,a]	35.23	32.92	3226
acetic acid (CH_3COOH)	57.30[12,a]	28.14	28.89	3237
cyclopropane (cyclo-C_3H_6)	61.54[31]	40.70	34.03	3405
propene (C_3H_6)	67.07[31]	35.17	33.78	3438
ethylene glycol ($(CH_2OH)_2$)	63.53[12,a]	36.75	37.00	3627
propionitrile (C_2H_5CN)	69.43[12,a]	37.36	34.40	3661
dimethyl sulfone ($(CH_3)_2SO_2$)	93.46[12,a]	39.13	42.69	3888
propionaldehyde (C_2H_5CHO)	70.65[12,a]	40.23	38.05	3893
acetone ($(CH_3)_2CO$)	70.91[12,d]	39.97	38.04	3925
propane (C_3H_8)	69.13[31]	47.95	42.09	3999
1-propanol (C_3H_7OH)	75.32[12,a]	50.40	46.26	4398
trimethylamine ($(CH_3)_3N$)	90.68[11]	45.79	50.39	4608
n-propylamine ($C_3H_7NH_2$)	85.68[12,a]	50.79	50.57	4655
butyraldehyde (C_3H_7CHO)	91.02[12,a]	53.94	51.44	5065
n-butane (C_4H_{10})	89.15[27]	62.01	55.49	5172
diethyl sulfide ($(C_2H_5)_2S$)	122.39[12,a]	61.09	61.29	5408
ethyl acetate ($H_3CCOOC_2H_5$)	95.91[12,a]	57.69	55.69	5550
dioxane ($C_4H_8O_2$)	95.69[12,b]	57.91	55.70	5424
diethyl ether ($(C_2H_5)_2O$)	97.14[12,a]	62.66	59.63	5548
diethylamine ($(C_2H_5)_2NH$)	106.93[12,a]	63.62	64.02	5810
cyclopentane (C_5H_{10})	101.48[12,d]	68.92	60.84	5840
n-pentane (C_5H_{12})	108.94[27]	76.30	69.00	6346
neopentane (C_5H_{12})	109.20[31]	76.04	68.99	6368
ethyl propyl ether ($C_2H_5OC_3H_7$)	117.78[12,d]	76.10	73.15	6721
ethyl propionate ($C_2H_5COOC_2H_5$)	115.83[12,a]	71.85	69.23	6725
1-bromohexane ($n-C_6H_{13}Br$)	160.67[12,a]	85.14	84.53	7394
cyclohexanol ($C_6H_{11}OH$)	128.62[12,a]	84.50	78.61	7465
n-hexane (C_6H_{14})	128.67[27]	90.65	82.59	7519
triethylamine ($(C_2H_5)_3N$)	148.88[12,a]	89.83	91.18	8136

TABLE 1 (Continued)

molecule	$10^{41}\alpha/\mathrm{C^2\,m^2\,J^{-1}}$	$10^{41}\Delta\alpha/\mathrm{C^2\,m^2\,J^{-1}}$	$10^{41}\Delta\alpha_{CR}/(\mathrm{C^2\,m^2\,J^{-1}})^{1/3}$	$D^{at}/\mathrm{kJ\,mol^{-1}}$
1-bromoheptane ($C_7H_{15}Br$)	180.59[12,a]	99.31	98.24	8567
diisopropyl ketone ($C_7H_{14}O$)	150.54[12,a]	96.66	92.20	8629
n-heptane (C_7H_{16})	148.42[27]	104.98	96.24	8693
n-octane (C_8H_{18})	168.18[27]	119.30	109.93	9866
2,2,4-trimethylpentane (C_8H_{18})	171.80[12,a]	115.68	109.85	9881
n-nonane (C_9H_{20})	193.16[12,a]	128.41	123.55	11038
n-decane ($C_{10}H_{22}$)	213.02[12,d]	142.63	137.31	12212
n-undecane ($C_{11}H_{24}$)	233.99[12,a]	155.74	151.08	13386
n-dodecane ($C_{12}H_{26}$)	253.74[12,d]	170.07	164.89	14558

[a] Experimental value is used. [b] Value, where experimental and theoretical value nearly coincide. [c] Mean between experimental and theoretical value. [d] Mean of experimental values.

TABLE 2: Dipole Polarizability α, Change of Dipole Polarizability Δα and $\Delta\alpha_{CR}$, and Atomization Energy D^{at} of Conjugated Compounds

molecule	$10^{41}\alpha/\mathrm{C^2\,m^2\,J^{-1}}$	$10^{41}\Delta\alpha/\mathrm{C^2\,m^2\,J^{-1}}$	$10^{14}\Delta\alpha_{CR}/(\mathrm{C^2\,m^2\,J^{-1}})^{1/3}$	$D^{at}/\mathrm{kJ\,mol^{-1}}$
thiophene (C_4H_4S)	100.14[12,a]	38.82	36.75	3901
furan (C_4H_4O)	80.45[12,a]	34.83	35.02	4023
1,3-butadiene (C_4H_6)	89.10[45]	32.38	38.68	4065
pyrrole (C_4H_5N)	88.35[12,c]	37.68	39.44	4244
pyridine (C_5H_5N)	105.37[12,b]	39.91	44.63	4961
p-dichlorobenzene ($C_6H_4Cl_2$)	157.66[12,a]	35.98	52.28	5392
benzene (C_6H_6)	111.77[41]	48.20	49.47	5526
cytosine ($C_4H_5N_3O$)	114.60[12,a]	44.01	52.84	5624
hexafluorobenzene (C_6F_6)	109.93[12,c]	42.12	47.94	5732
aniline (C_6H_7N)	128.57[12,a]	50.79	58.11	6166
thymine ($C_5H_6N_2O_2$)	124.95[12,c]	57.00	62.01	6334
toluene (C_7H_8)	136.69[12,d]	57.36	62.93	6694
styrene (C_8H_8)	160.34[12,a]	52.95	68.10	7330
p-nitrotoluene ($C_7H_7NO_2$)	156.89[12,a]	58.99	71.98	7438
p-xylene (C_8H_{10})	157.00[12,d]	71.13	76.58	7895
N,*N*-dimethylaniline ($C_8H_{11}N$)	170.40[12,d]	77.12	85.39	8459
naphthalene ($C_{10}H_8$)	195.72[12,a]	56.05	78.84	8761
1,3,5-trimethylbenzene (C_9H_{12})	179.58[12,c]	82.63	90.23	9056
ferrocene ($Fe(C_5H_5)_2$)	208.0[23]	152.6	96.8	9534
osmocene ($Os(C_5H_5)_2$)	228.4[23]	132.8	96.4	9774
hexamethylbenzene ($C_{12}H_{18}$)	231.55[12,c]	132.90	131.68	12611

[a] Experimental value is used. [b] Value, where experimental and theoretical value nearly coincide. [c] Mean between experimental and theoretical value. [d] Mean of experimental values.

TABLE 3: Dipole Polarizability α, Change of Dipole Polarizability Δα and $\Delta\alpha_{CR}$, and Atomization Energy D^{at} of Alkali-Metal Diatoms

molecule	$10^{41}\alpha/$ $\mathrm{C^2\,m^2\,J^{-1}}$	$10^{41}\Delta\alpha/$ $\mathrm{C^2\,m^2\,J^{-1}}$	$10^{13}\Delta\alpha_{CR}/$ $(\mathrm{C^2\,m^2\,J^{-1}})^{1/3}$	$D^{at}/$ $\mathrm{kJ\,mol^{-1}}$
Cs_2	704[25]	396	16.7	43.9
Rb_2	757[25]	445	16.7	48.9
K_2	679[25]	327	15.3	54.6
Na_2	334[25]	203	12.8	73.6
Li_2	378[25]	111	11.4	110.2

In the case of the molecules we refer mostly to the original literature or to the compilations given by Miller.[12] If possible, zero-frequency (static) dipole-polarizabilities α(0) obtained in the gas phase are used. This cancels the effects of intermolecular interactions and frequency dispersion on the polarizability. If calculated polarizabilities are used only converged data which are (nearly) independent of basis sets and methods are taken into account. It must be stressed, that only the electronic part of the dipole-polarizability is considered here. The vibrational contribution most prominent in the IR-spectral region and at zero frequency is not taken into account.

In Table 1 the molecules considered, their dipole-polarizability α, the change in the dipole-polarizability $\Delta\alpha \equiv \Sigma_i\nu_i\alpha_i$, the change of the cube-root of the polarizability $\Delta\alpha_{CR} \equiv \Sigma_i\nu_i\alpha_i^{1/3}$, and the atomization energy D^{at} are given for compounds without conjugated double bonds or aromatic systems. In Table 2 the same data are shown for conjugated systems, whereas Table 3 shows the results for the alkali-dimers. The data of Tables 1−3 are plotted in Figures 1 and 2. A clear correlation between D^{at} and Δα as well as $\Delta\alpha_{CR}$ is observed.

3. Results and Discussion

First we will deal with the molecules given in Table 1. For these molecules a least-squares fit yields the parameters of the relations

$$D^{at} = A_1 + B_1\Delta\alpha \tag{4}$$

and

$$D^{at} = A_{1/3} + B_{1/3}\Delta\alpha_{CR} \tag{5}$$

as $A_1 = (501 \pm 45)$ kJ mol^{-1}, $B_1 = (8.134 \pm 0.078) \times 10^{45}$ V^2 m^{-2} mol^{-1}, and $A_{1/3} = (295 \pm 43)$ kJ mol^{-1}, $B_{1/3} = (8.746 \pm 0.078) \times 10^{18}$ (J^4 mol^{-3} C^{-2} m^{-2})$^{1/3}$, respectively. The correlation coefficients are $r = 0.9963$ and 0.9968, respectively. In both cases the data are described by straight lines with good accuracy. The situation changes if conjugated double bonds or aromatic systems are considered (Table 2). In this case we obtain $A_1^C = (3.22 \pm 0.55) \times 10^3$ kJ mol^{-1}, $B_1^C = (5.68 \pm 0.76) \times 10^{45}$ V^2 m^{-2} mol^{-1}, and $A_{1/3}^C = (9.4 \pm 1.9) \times 10^2$ kJ mol^{-1}, $B_{1/3}^C = (9.07 \pm 0.27) \times 10^{18}$ (J^4 mol^{-3} C^{-2} m^{-2})$^{1/3}$, respectively. The correlation coefficients are $r = 0.8637$ and 0.9916, respectively. The superscript "*C*" denotes the case of conjugated double bonds. It is obvious, that D^{at} vs Δα hardly follows a

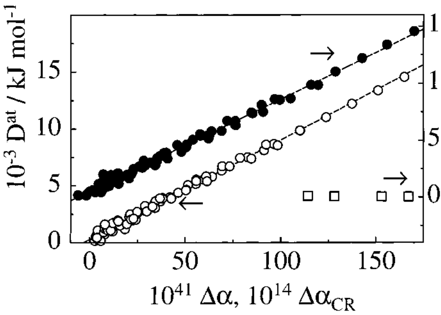

Figure 1. Atomization energy D^{at} in dependence of $\Delta\alpha$ (●, right scale) and $\Delta\alpha_{CR}$ (○, left scale) for the reactions given in Table 1. $\Delta\alpha_{CR}$ of Table 3 (alkali-metal diatoms, □) refer to the right scale. The dashed lines are the results from the least-squares fit. $\Delta\alpha$ is given in units of $C^2\ m^2\ J^{-1}$, whereas $\Delta\alpha_{CR}$ is in $(C^2\ m^2\ J^{-1})^{1/3}$. Two scales are used because otherwise the data points accidentally are indistinguishable.

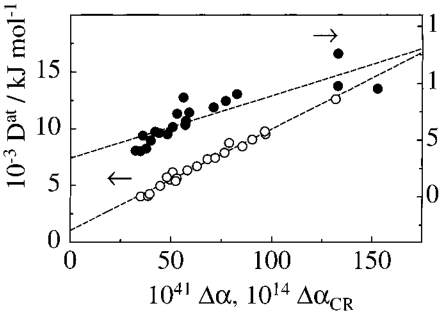

Figure 2. Same plot as in Figure 1 for the molecules of Table 2.

straight line. On the other hand D^{at} vs $\Delta\alpha_{CR}$ still shows a linear behavior. Additionally within the error bounds we observe $B_{1/3} \approx B^{C}_{1/3}$.

Obviously, the minimum polarizability principle is not always valid. In the case of the diatomics fluorine, chlorine, bromine, iodine, and oxygen the polarizability of the reactant is higher than the sum of α of the products, although the products have a higher total energy. For all other molecules the MPP is valid. It must be stressed that all species are supposed to be in their ground state. On the other hand we found that $\Delta\alpha_{CR}$ is always positive. This clearly shows that $\Delta\alpha_{CR}$ gives an indication for the most stable species. Taking into account the proportionality $\alpha^{1/3} \sim 1/\eta$, which was, however, only observed in the case of atoms,[10] our findings can be called an approximate maximum hardness principle, AMHP. In Table 3 results for the alkali-metal diatoms are given. We observe that the AMHP is valid, since $\Delta\alpha_{CR} > 0$. However, these data do not fit to the other results presented in Tables 1 and 2 which are displayed in Figures 1 and 2.

Case of Isomers. Consider molecules M_1 and M_2 to be two isomers with necessarily the same sum-formula A_mB_n.... Their standard enthalpies of formation are $\Delta_f H_1^0$ and $\Delta_f H_2^0$ and the respective polarizabilities α_1 and α_2. It follows that the terms $\sum_p \Delta_f H_p^0$, $\sum_p \nu_p \alpha_p$, and $\sum_p \nu_p {\alpha_p}^{1/3}$, respectively, are the same for both isomers. p denotes all products. Assuming the validity of eqs 4 and 5 we obtain for

$$-\Delta_f H_1^0 + \Delta_f H_2^0 = B_1(\alpha_2 - \alpha_1) \tag{6}$$

and

$$-\Delta_f H_1^0 + \Delta_f H_2^0 = B_{1/3}({\alpha_2}^{1/3} - {\alpha_1}^{1/3}) \tag{7}$$

Let molecule M_1 be the thermodynamically more stable isomer, then we have $\Delta_f H_1^0 < \Delta_f H_2^0$. This implies immediately $\alpha_2 > \alpha_1$, which means that the thermodynamically more stable isomer has the lower polarizability. This phenomenon was also observed by Doerksen and Thakkar[28] in their extensive systematic theoretical study of the dipole polarizability and energy of azaborinines, azaboroles and oxazaboroles. Taking into account calculations on 70 molecules they conclude that *the most stable isomer is the least polarizable*.[28] Beside some few exceptions the same observation was made by Ghanty and Ghosh[5] who have calculated the polarizability, hardness and energy of several small molecules. The minimum polarizability principle is also found in intramolecular changes of the geometry. Chattaraj et al.[4] have observed that asymmetric distortions of the equilibrium geometry in small molecules such as NH_3 and H_2S always lead to an increase in the polarizability. The same observation is made for torsional motions in HOOH, HSSH, HSOH, and C_2H_4. The equilibrium geometry always possesses the minimal polarizability with respect to rotational motions.

Although eqs 4 and 5 are not ecaxtly fulfilled this statement should be observable for isomeric molecules listed in Table 1. The minimum polarizability principle is found to be valid for the isomers dimethyl sulfide and ethanethiol, dimethyl ether and ethanol, and trimethylamine and *n*-propylamine. In the first two examples, however, the polarizability differences are very small and definitely smaller than the uncertainties of the polarizability values of the compounds. The minimum polarizability principle between isomers does not hold in the case of ethylene oxide and acetaldehyde, propionaldehyde and acetone, ethyl acetate and dioxane, *n*-pentane and neopentane, and *n*-octane and 2,2,4-trimethylpentane. Again it must be noted that the polarizability differences are in the order of the uncertainties of the polarizability values. An exceptional case is definitely the pair propene and cyclo-propane. Both, the polarizabilities and the heats of formation are known with high accuracy. Nevertheless, the more stable isomer propene has a higher polarizability than cyclopropane.

Chemical Reactions. In the case of complete fragmentations we have observed that the sign of $\Delta\alpha_{CR}$ gives an indication of the direction to which a chemical reaction evolves. We write a chemical reaction in the compact form $\sum_i \nu_i M_i = 0$. i runs over all participants M_i of the reaction. From eq 5 it follows that the enthalpy of this reaction $\Delta_R H^0$ can be written as

$$\Delta_R H^0 = B_{1/3} \sum_i \nu_i {\alpha_i}^{1/3} \tag{8}$$

If the products are more stable than the reactants we have $\Delta_R H^0 < 0$. This implies that $\sum_i \nu_i {\alpha_i}^{1/3} < 0$, too. In Table 4 several chemical reactions are considered, some of them are just hypothetical. In most cases we see that the thermodynamically more stable products have the lower sum of the cube-root of the polarizabilities. Beside the two reactions with hydrazine and hydrogencyanide, respectively, there is one severe exception. In the case of the highly exothermic reaction $H_2 + Cl_2 \rightarrow 2HCl$ all polarizabilities are known with high accuracy. Nevertheless, this reaction does not produce the products with the lowest sum of $\alpha^{1/3}$.

Chattaraj et al.[4] have shown that the minimum polarizability principle and the maximum hardness principle are also valid in the case of double proton-transfer reactions. Ghanty and Ghosh[5] have considered a number of exchange reactions. By considering the hardness η and the cube root of the polarizability $\alpha^{1/3}$ they found that exchange reactions tend to proceed in the direction of a minimal sum of $\alpha^{1/3}$. This observation is in accordance with our findings. Gázquez[9] made a similar observation and found that exchange reactions go in the direction of maximal

TABLE 4: Chemical Reactions and Corresponding Change of $\alpha^{1/3}$ [a]

reaction	$10^{14}\Delta\alpha_{CR}$/ $(C^2 m^2 J^{-1})^{1/3}$	$\Delta_R H^0$/ kJ mol^{-1}
$2NO \rightarrow N_2 + O_2$	−0.1	−18
$2NO_2 \rightarrow N_2O_4$	−4.8[b]	−47
$(CH_3)_2O + H_2S \rightarrow H_2O + (CH_3)_2S$	−0.8	−73
$CH_3F + CHF_3 \rightarrow CH_4 + CF_4$	−0.3	−88
$C_2H_2 + CH_4 \rightarrow C_3H_6$ (propene)	−5.1	−131
$C_2H_4O + H_2 \rightarrow (CH_3)_2O$	−4.1	−132
$H_2 + O_2 \rightarrow H_2O_2$	−3.8	−135
$4H_2 + CO_2 \rightarrow 2H_2O + CH_4$	−7.1	−148
$2OH \rightarrow H_2O_2$	−3.7[c]	−213
$H_2 + CO \rightarrow CH_2O$	−4.0	−215
$Cl_2 + C_2H_2 \rightarrow H_2CCCl_2$	−5.6	−230
$C_2H_6 + O_2 \rightarrow (CH_2OH)_2$	−4.7	−312
$(CH_3)_2S + O_2 \rightarrow (CH_3)_2SO_2$	−5.2	−335
$2H_2 + O_2 \rightarrow 2H_2O$	−3.7	−467
$2CO + O_2 \rightarrow 2CO_2$	−4.4	−567
$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$	+3.8	−652
$CO + NH_3 \rightarrow H_2O + HCN$	−0.3	+49
$H_2 + Cl_2 \rightarrow 2HCl$	+0.8	−185

[a] Some of the reactions are hypothetical. [b] Polarizabilities taken from ref 46. [c] Polarizabilities taken from ref 47.

hardness or highest average hardness. Hati and Datta[10] observed that the thermodynamic stability of a chemical system increases with the increase in the value of hardness. From this we can also conclude that the thermodynamic stability increases with decreasing values of $\sum \nu_i \alpha_i^{1/3}$.

Fit Parameters A_1 and B_1. We will finish our discussion by considering the fit parameters A_1 and B_1 of eq 4. The term B_1/N_A ($N_A = 6.0221367 \times 10^{23}$ mol^{-1} is Avogadro's constant) has the unit of a squared field strength E^2. It is therefore obvious to write $B_1/N_A = E^2/2$. $\Delta\alpha E^2/2$ can now be thought of as some sort of potential energy which results from the change of the polarizability of the reacting species in the presence of the electrical field with field strength E. We yield $E = 1.644 \times 10^{11}$ V/m. E is in the order of the atomic field strength of $E_0 = E_h/(ea_0) = 5.14 \times 10^{11}$ V/m ($E_h = 4.3597482 \times 10^{-18}$ J and $a_0 = 5.29177249 \times 10^{-11}$ are the atomic units of energy and length, respectively, and $e = 1.60217733 \times 10^{-19}$ C is the elementary charge). The magnitude of E is nearly exactly the same as the field strength of the "chemical reaction field" (that is the field created by all atoms taking part in a chemical reaction) introduced by Chattaraj and Nath[1] in their calculations of the electronegativity dynamics during the course of a chemical bond forming reaction. E found in this work is about 10 times the field strength observed, e.g., in vacancies of zeolithes[35] and ice clusters.[36] In these vacancies only physisorption takes place whereas chemical reactions are governed by higher field strengths produced by the chemical reaction field.

The term A_1/B_1 has the unit of a dipole-polarizability. We obtain $A_1/B_1 = (6.16 \pm 0.56) \times 10^{-41}$ C^2 m^2 J^{-1}. A_1/B_1 is in the order of the polarizability of the hydrogen atom. More possible explanations for these observations in terms of the virial theorem and the concept of atoms in molecules were already given by Hohm.[29] They will not be repeated here.

It must be stressed that eqs 4 and 5 cannot be used to predict atomization energies from polarizability data. Generally, the polarizabilities are not known with sufficient accuracy. However, these two equations may be used to estimate polarizabilities from known thermochemical data. The accuracy of the so determined polarizabilities lies in the range between 2 and 10%.

4. Conclusions

We have shown that in complete fragmentations $A_mB_n... \rightarrow mA + nB + ...$ the sign of the term $\Delta\alpha_{CR} \equiv \sum_i \nu_i \alpha_i^{1/3}$ gives an indication for the higher thermodynamic stability of the reactant. On the other hand the sign of $\Delta\alpha \equiv \sum_i \nu_i \alpha_i$ does not provide a clear indication of thermodynamic stability. This makes the averaged maximum hardness principle (AMHP) which is obtained by considering $\alpha^{1/3}$ to be more suitable than the minimum polarizability principle (MPP). Additionally, we observed the atomization energy to depend nearly linearly on $\Delta\alpha_{CR}$. This relationship implies also the AMHP to be valid in the case of other chemical reactions. It is already known that this holds also true for the maximum hardness principle, MHP. To prove these principles for isomeric molecules, however, more precise data on the polarizability of atoms and molecules are needed. This is also obvious by considering the literature (e.g., ref 5), where a comparison of the existing data on energy, hardness and polarizability of isomeric molecules does not give an unambiguous prove of any of the three principles (AMHP, MPP, and MHP).

References and Notes

(1) Chattaraj, P. K.; Nath, S. *Int. J. Quantum Chem.* **1994**, *49*, 705.
(2) Chattaraj, P. K.; Sengupta, S. *J. Phys. Chem.* **1996**, *100*, 16126.
(3) Chattaraj, P. K.; Poddar, A. *J. Phys. Chem. A* **1998**, *102*, 9944.
(4) Chattaraj, P. K.; Fuentealba, P.; Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **1999**, *103*, 9307.
(5) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1996**, *100*, 12295.
(6) Chandra, A. K.; Uchimura, T.; Sugie, M.; Sekiya, A. *Chem. Phys. Lett.* **2000**, *318*, 69.
(7) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.
(8) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854.
(9) Gázquez, J. L. *J. Phys. Chem. A* **1997**, *101*, 9464.
(10) Hati, S.; Datta, D. *J. Phys. Chem.* **1994**, *98*, 10451.
(11) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1995.
(12) Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533.
(13) Maroulis, G.; Hohm, U. *Polarizabilities. A User's Guide*; Kluwer Academic Publishers: Dordrect, in preparation.
(14) Koide, A.; Meath, W. J.; Allnatt, A. R. *J. Phys. Chem.* **1982**, *86*, 1222.
(15) Das, A. K.; Thakkar, A. J. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 2215.
(16) Hohm, U.; Loose, A.; Maroulis, G.; Xenides, D. *Phys. Rev. A* **2000**, *61*, 053202.
(17) Stiehler, J.; Hinze, J. *J. Phys. B: At. Mol. Opt. Phys.* **1995**, *28*, 4055.
(18) Maroulis, G.; Makris, C.; Hohm, U.; Goebel, D. *J. Phys. Chem. A* **1997**, *101*, 953.
(19) Chamberlain, G. E.; Zorn, J. C. *Phys. Rev.* **1963**, *129*, 677.
(20) Ekstrom, C. R.; Schmiedmayer, J.; Chapman, M. S.; Hammond, T. D.; Pritchard, D. E. *Phys. Rev. A* **1995**, *51*, 3883.
(21) Hall, W. D.; Zorn, J. C. *Phys. Rev. A* **1974**, *10*, 1141.
(22) Bonin, K. D.; Kadar-Kallen, M. A. *Phys. Rev. A* **1993**, *47*, 944.
(23) Goebel, D.; Hohm, U. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3467.
(24) Jhanwar, B. L.; Meath, W. J. *Chem. Phys.* **1982**, *67*, 185.
(25) Molof, R. W.; Miller, T. M.; Schwartz, H. L.; Bederson, B.; Park, J. T. *J. Chem. Phys.* **1974**, *61*, 1816.
(26) Maroulis, G. *Mol. Phys.* **1997**, *91*, 333.
(27) Jhanwar, B. L.; Meath, W. J.; MacDonald, J. C. F. *Can. J. Phys.* **1981**, *59*, 185.
(28) Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem. A* **1999**, *103*, 2141.
(29) Hohm, U. *J. Chem. Phys.* **1994**, *101*, 6362.
(30) Hohm, U. *Z. Naturforsch. A* **1993**, *48*, 505.
(31) Hohm, U. *Mol. Phys.* **1993**, *78*, 929.
(32) Hohm, U.; Trümper, U. *J. Raman Spectrosc.* **1995**, *26*, 1059.
(33) Hohm, U. *Mol. Phys.* **1999**, *96*, 7.
(34) Zeiss, G. D.; Meath, W. J.; MacDonald, J. C. F.; Dawson, D. J. *Can. J. Phys.* **1977**, *55*, 2080.
(35) Kahn, R.; Cohen De Lara, E.; Möller, K. D. *J. Chem. Phys.* **1985**, *83*, 2653.
(36) Batista, E. R.; Xantheas, S. S.; Jonsson, H. *J. Chem. Phys.* **2000**, *112*, 3285.
(37) Maroulis, G.; Thakkar, A. J. *J. Chem. Phys.* **1989**, *90*, 366.

(38) Maroulis, G. *J. Chem. Phys.* **1992**, *96*, 6048.
(39) Maroulis, G.; Pouchan, C. *Chem. Phys.* **1997**, *215*, 67.
(40) Maroulis, G.; Pouchan, C. *Phys. Rev. A* **1998**, *57*, 2440.
(41) Kumar, A.; Meath, W. J. *Mol. Phys.* **1992**, *75*, 311.
(42) Kumar, A.; Meath, W. J. *Can. J. Chem.* **1985**, *63*, 1616.
(43) Goebel, D.; Hohm, U. *Chem. Phys. Lett.* **1997**, *265*, 638.
(44) Maroulis, G. *Mol. Phys.* **1992**, *76*, 1303.
(45) Maroulis, G.; Makris, C.; Hohm, U.; Wachsmuth, U. *J. Phys. Chem. A* **1999**, *103*, 4359.
(46) Goebel, D.; Hohm, U.; Kerl, K.; Trümper, U.; Maroulis, G. *J. Phys. Chem.* **1994**, *98*, 13123.
(47) Spelsberg, D. *J. Chem. Phys.* **1999**, *111*, 9625.