MO ANALYSIS OF CHEMICALLY INTERACTING SYSTEMS. REACTION OF HYDROGEN ABSTRACTION BY FREE RADICALS

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The charge and spin transfer accompanying the process of the exchange of the bonds in the reaction of hydrogen abstraction by free radicals was examined in terms of intermolecular population analysis. The results obtained enable a qualitative discussion of the role of polar and steric effects in this reaction.

Among the commonest, and also the most extensively studied, transfer reactions of radicals belong the so-called H-abstraction. The significance of reactions of this kind in a number of industrially important processes has stimulated an ever-increasing interest in their basic kinetic and thermodynamic characteristics. The results have been summarized in several reviews, the most important of which are, *e.g.*, in refs[1-3]. The increasing availability of reliable experimental data have stimulated the interest of theoretical chemists in elucidating the fundamental factors controlling the course of these reactions. Although the treatment employing diverse static indices of chemical reactivity enabled some stereoselectivity and relative reactivity problems to be cleared up[4-8], it was only the recent development of numerical methods in quantum chemistry that led to attempts at a really immediate quantitative confrontation of the various theoretical data with the corresponding experimental characteristics. This concerns, for instance, direct calculations of the structures of transition states and activation barriers, reaction rates[9-18], or the kinetic isotopic effect[19]. These direct approaches start to be still more frequently complemented by some new techniques allowing the language of quantum chemical results to be translated into qualitative but chemically much more comprehensible characteristics. Into the framework of such effort can be included *e.g.* the work by Fueno and his coworkers[20] or Fujimoto and coworkers[21,22], who employed the so-called configuration analysis approach[23] for studying the nature of intermolecular interactions between a molecule and an attacking radical in the transition state. An alternative approach to the description of intermolecular interactions, whereby the energy aspect can be included, consists of the use of the so-called Morokuma's decomposition[24,25].

An interesting theoretical possibility for the classification of attacking radical species from the point of view of their electrophilic or nucleophilic nature has been opened up by the study[26].

All these approaches, which analyze the nature of interactions between reacting molecules from various aspects, can be complemented conveniently with the technique of the so-called intermolecular population analysis[27], which enables us, by

relatively simple means to gain insight into the process of the formation and the exchange of the bonds occurring during the reactive chemical interaction. Elaborated from a general point of view by Hoffmann and Fujimoto, this technique has been used recently for the analysis of radical addition reactions[28,29]. The usefulness of the results of these studies led us to extend them to the reaction of hydrogen abstraction.

THEORETICAL

Since the method of intermolecular population analysis has been sufficiently described elsewhere[27], we shall confine ourselves to a brief presentation of the basic terms as are necessary for the purposes of this study. The method is based on a description of the density function ϱ of the interacting supermolecule A ... B in terms of densities ϱ_A, ϱ_B of the isolated fragments. The distortion of the electronic structure $\Delta\varrho$ during the interaction of the fragments A, B is expressed as

$$\Delta\varrho = \Delta\varrho_A + \Delta\varrho_B + \varrho_{AB}, \qquad (1)$$

where the first two right-hand terms refer to the redistribution of the electron density within the isolated fragments (polarization) and the last term refers to the mutual interaction of molecules A, B resulting in the disappearance of old bonds and formation of new ones. This bond exchange process can be globally characterized with the aid of the so-called intermolecular population V_{AB}, defined as the integral of the interaction density ϱ_{AB},

$$V_{AB} = \int \varrho_{AB}(1) \, d\tau(1). \qquad (2)$$

Positive V_{AB} correspond to the attractive interactions between the reactants, negative V_{AB} correspond to a repulsive effect.

In addition to this global characteristics, some interesting conclusions concerning the nature of the reactive interaction can be derived from a formal decomposition of the total populations V_{AB} into contributions corresponding to the various interaction mechanisms such as exchange repulsion, charge transfer, *etc*. This form of decomposition allows the results of the abstract quantum chemistry language to be transformed into a more illustrative description based on classical chemical concepts. For instance, the exchange repulsion contribution corresponds roughly to what is classically understood as the so-called steric effect. Similarly, the charge tranfer contributions give some notion of the magnitude of polar effects. By comparing these contributions with suitable experimental characteristics it is thus possible to gain insight, for each particular case, into factors taking part in the interaction of the corresponding molecular species. In the present case, this approach was applied to the analysis of the reaction of hydrogen abstraction from methane by a series

of radicals of different polarity,

$$CH_3\!-\!H + X^{\bullet} \rightarrow [CH_3...H...X]^{\neq} \rightarrow CH_3^{\bullet} + H\!-\!X \qquad (A)$$
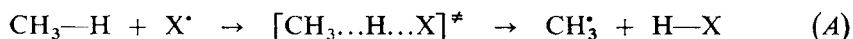
with $X^{\bullet} = H^{\bullet}$, $CH_3^{\bullet}$, $NH_2^{\bullet}$, $OH^{\bullet}$, $F^{\bullet}$. For all of them both the experimental activation energies and structures of the transition states determined at the SCF level by *ab initio* calculations in the $6-31G$ basis were available[15]. Disregarding inaccuracies in the structures of the calculated transition states that may emerge from the possible inadequacy of the $6-31G$ basis to the calculation of radical species in particular (see, *e.g.*, the comparison of the theoretical and experimental activation energies in ref.[15]), we used the geometrical parameters of the structures as the input data for the subsequent population analysis based on EHT molecular orbitals. This method is actually the only one (apart from the *ab initio* techniques) that takes into account the overlap during the normalization of the molecular orbitals, which is a prerequisite for a reliable description of the intermolecular interactions.

The analysis consists in the transformation of the molecular orbitals of the interacting supermolecule A...B from the conventional basis of atomic orbitals into the basis of molecular orbitals of fragments A and B. The intermolecular populations V_{AB} then can be expressed *via* the intermolecular overlap integrals S_{il} and the corresponding coefficients L_{nk} by Eq. (3)

$$V_{AB} = \sum_i^{(A)} \sum_l^{(B)} V_{ABi,l}, \qquad (3a)$$

$$V_{ABi,l} = 4 \sum_n^{occ} L_{ni} L_{nl} S_{il}. \qquad (3b)$$

The individual components corresponding to exchange repulsion, charge transfer, *etc.*, then can be obtained by a suitable choice of the summation limits in Eq. $(3a)$. For instance, by summation over the occupied orbitals of the two fragments only, the exchange repulsion contribution is obtained; summation over the occupied orbitals of fragment A and free orbitals of fragment B provides the A → B charge transfer contribution; *etc.* The philosophy of this approach, based on the combination of different quantum chemical methods which, moreover, are of rather different quality is not stimulated only by economical reasons but above all reflects the fact that our aim does not consist in the exact reproduction of some experimental quantities but rather in the qualitative elucidation of the trends manifesting themselves in a given series of reactions differing by the systematic variation of some structural parameters. The adequacy of this approach is not only felt intuitively but it is also warranted by some numerical comparisons[29] giving evidence that EHT population analysis reproduces closely the trends found by more sophisticated *ab initio* methods.

RESULTS AND DISCUSSION

The calculated values of intermolecular populations and their components are given in Table I for the series of reactions studied.

The calculated characteristics can be compared with experimental data at various levels. The coarsest consists of a mere qualitative discussion of the conclusions following for the process of bond exchange from the calculated intermolecular populations and their components. In our case the mutual comparison of the total populations V_{AB} points to an overall attractive nature of the interaction between methane and the attacking radical in all cases. A more detailed decomposition of the

TABLE I

Calculated values of total populations V_{AB} and their components in the reaction of hydrogen abstraction from methane by a series of radicals X of different polarity

Reaction		Component	α spin	β spin	total
A B		exch. rep.	−0·2018	−0·0926	−0·2944
$CH_4 + CH_3^\bullet$		A → B	0·0054	0·1798	0·1852
		B → A	0·2004	0·0342	0·2346
		virt.	−0·0007	0·0026	0·0019
		V_{AB}	0·0033	0·1240	0·1273
A B		exch. rep.	−0·1366	0·0159	−0·1207
$CH_4 + NH_2^\bullet$		A → B	−0·0020	0·1346	0·1326
		B → A	0·1863	0·0386	0·2249
		virt.	−0·0002	0·0112	0·0110
		V_{AB}	0·0475	0·2005	0·2478
A B		exch. rep.	−0·1105	−0·0008	−0·1113
$CH_4 + OH^\bullet$		A → B	−0·0074	0·1044	0·0970
		B → A	0·1495	0·0324	0·1719
		virt.	0·0006	0·0269	0·0275
		V_{AB}	0·0322	0·1629	0·1951
A B		exch. rep.	−0·1504	0	−0·1504
$CH_4 + H^\bullet$		A → B	0	0·2526	0·2526
		B → A	0·2549	0	0·2549
		virt.	0	0·0408	0·0408
		V_{AB}	0·1045	0·2934	0·3979
A B		exch. rep.	−0·0992	0·0604	−0·0388
$CH_4 + F^\bullet$		A → B	0	−0·0001	−0·0001
		B → A	0·0849	0·0452	0·1301
		virt.	0	0·0001	0·0001
		V_{AB}	−0·0143	0·1056	0·0913

total populations V_{AB} into components corresponding to α and β spin demonstrates that it is basically the contribution of electrons with β spin that is responsible for the attractive nature of the interaction and thus, roughly speaking, for the formation of new bonds in the $CH_3...H...X$ complex. This result bears out the results of some recent analyses[21,22,26]. At the same time, however, the data of Table I indicate that rather than to an overall weak engagement of electrons with α spin in the bond exchange process, the negligible V_{AB} contributions are due to the contribution of the charge transfer from the radical (where the unpaired electron has α spin) to the molecule of methane $(B \rightarrow A)_\alpha$ being just nearly compensated by the exchange repulsion contribution. For the electrons with β spin, on the other hand, the exchange repulsion contribution is not high enough to compensate for the charge transfer from the molecule to the radical $(A \rightarrow B)_\beta$, so that the net outcome is an attractive effect.

These qualitative conclusions also apply at a quantitative level in that, for instance, satisfactory linear correlations exist between the experimental activation energies in the series of reactions studied (Table VI in ref.[15]) and the charge transfer contributions. The correlations of the experimental activation energies with the exchange repulsion contributions, however, are much poorer. The obtained regression equations along with the correlation coefficients are as follows:

$$E_a = 102 \cdot 65(B \rightarrow A)_{tot} - 12 \cdot 64 \quad r = 0 \cdot 953 \tag{4a}$$

$$E_a = 51 \cdot 13(A \rightarrow B)_{tot} + 1 \cdot 40 \quad r = 0 \cdot 881 \tag{4b}$$

$$E_a = 34 \cdot 77[(A \rightarrow B)_{tot} + (B \rightarrow A)_{tot}] - 3 \cdot 48 \quad r = 0 \cdot 915 \tag{4c}$$

$$E_a = -49 \cdot 07(EXCH)_{tot} + 1 \cdot 19 \quad r = 0 \cdot 838 \tag{4d}$$

Since this treatment encompasses a relatively small data set $(n = 5)$, the statistical significance of the correlations is to be considered. The correlation coefficients show that correlations $(4a)-(4c)$ can be regarded as statistically significant at the $h = 95\%$ level, correlation $(4a)$ being even significant at the $h = 99\%$ level. Correlation $(4d)$ exhibits the lowest significance, $h = 92\%$. The plots in Fig. 1 show that correlations $(4a)-(4c)$ would actually be considerably closer but for the departing point for $X = H$. The cause of this systematic deviation can not be so far specified safely; it is even conceivable that there is some error involved in the experimental value, as suggested by Leroy and co-workers[16] based on a confrontation of the theoretical and experimental activation energies. Irrespective of the possible doubts concerning the reliability of the experimental value of the activation energy for the abstraction by the hydrogen atom, the correlation equations clearly indicate that polar effects play the major role in the hydrogen abstraction process whereas the effects of steric nature manifest themselves to a considerably lesser extent. This is consistent with

what can be expected based on the classical concepts; actually, there is no reason why steric effects should play a substantial role in the reactions under study. The significant role of the charge transfer contributions, indicated by the theory, makes it also possible to theoretically explain some empirical correlations, *e.g.*, between the activation energy and the Pauling electronegativity of the central atom M in the $MH_n^{\bullet}$ radical. In fact, we feel intuitively that the magnitude of these charge transfer terms will depend to a high degree on the polarity differences between the CH_4 molecule and the attacking radical. Since in our case the CH_4 molecule is the invariable component in the series, only the electronegativity of the attacking radical will appear as the decisive factor.
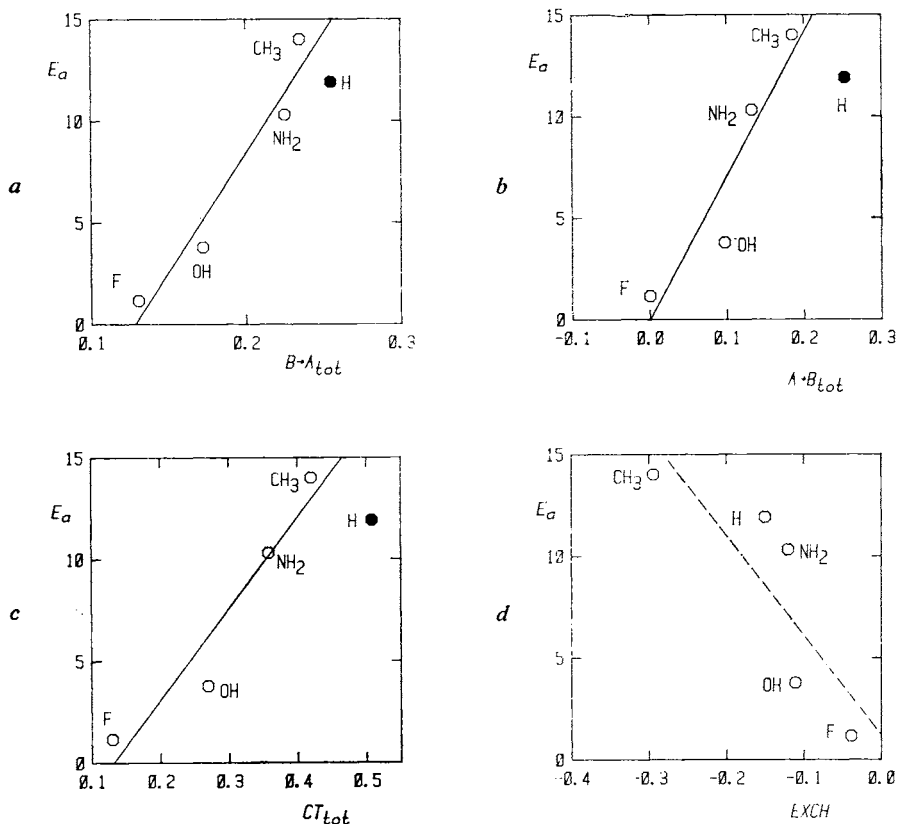

FIG. 1

Correlation of the experimental activation energies with the contributions corresponding to the charge transfer from the radical to methane (*a*), with the contributions corresponding to the charge transfer from methane to the radical (*b*), with the total charge transfer from methane to the radical and *vice versa* (*c*), and with the contributions corresponding to the exchange repulsion (*d*)

Another empirical correlation the validity of which has been frequently confirmed in the chemistry of radical abstraction reactions is the Bell–Evans–Polanyi relationship[30] between the activation energy and the reaction heat.

$$E_a = \alpha \, \Delta H + \beta \, . \tag{5}$$

The great majority of observed correlations of this kind pertain to a situation where the varied component in the reaction system is the closed-shell R—H molecule (due to variation of fragment R) while the abstracting radical is constant over the series treated. If in this case, described by the schematic Eq. (B)

$$R_i\text{—H} + X^{\bullet} \; \rightarrow \; R_i^{\bullet} + H\text{—X} \tag{B}$$
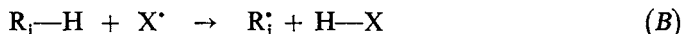
use is made of the approximation where the reaction heat is replaced by the corresponding reaction energy, ΔH can be estimated via a simple thermodynamic cycle using the energies E_i of the individual reaction components (Eq. 6)

$$\Delta H_i \approx E_{R_i^{\bullet}} + E_{H-X} - E_{X^{\bullet}} - E_{R_i-H} \tag{6}$$

or alternatively, via the bond dissociation energies as

$$\Delta H_i \approx D(R_i\text{—H}) - D(H\text{—X}) \, . \tag{7}$$

The validity of the corresponding Bell–Evans–Polanyi relation between E_a and the dissociation energy of the dissappearing R_i—H bonds has been really confirmed empirically in several papers[1,3,16,31]. In contrast to cases described by Eqs (B) and (7), however, considerably fewer correlations have been found in cases where the varied component was the attacking radical rather than the R—H molecule (Eq. (A)). Here the reaction heat can be approximated as

$$\Delta H_i \approx D(H\text{—}X_i) - D(CH_3\text{—}H) \, . \tag{8}$$

This relation indicates that the corresponding Evans–Polanyi equation will be a correlation between the activation energy and the bond dissociation energy of the newly forming H—X bond. In our case the particular form of this correlation is

$$E_a = -0.387D(H\text{—}X_i) + 54.62 \quad r = 0.925, n = 5 \, . \tag{9}$$

This is probably the first observed Evans–Polanyi relation describing the effect of polarity of the variable radical X on the abstraction of hydrogen from a C—H bond of methane.

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Translated by P. Adámek.