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A MNDO STUDY OF OLEFIN EPOXIDATION BY PEROXYACIDS. HAMMOND EFFECTS ON THE COMPUTED TRANSITION STRUCTURES

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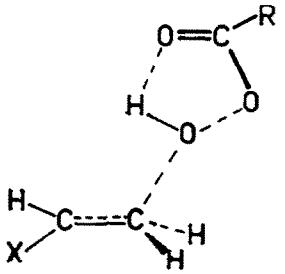
Abstract - MNDO calculations of potential energy surfaces for the interaction between peroxyformic acid and ethylene or substituted ethylenes do not support the electrophilic mechanism preferred in the interpretation of this reaction. While the calculated interaction between neutral molecules of olefin and peroxyformic acid is repulsive over the entire range of studied reaction coordinates, protonated peroxyformic acid is predicted capable of addition to olefin, but with an activation energy of 39 kcal/mol. Peroxyformate anions, according to the MNDO calculations, should add readily to olefins. Electron withdrawing substituents in the latter have the effect that adducts are formed without activation energy, while ethylene or olefins with donor substituents are predicted to react in a two-step mechanism, the first step being the formation of metastable intermediates with activation energies of 16 - 20 kcal/mol. The rate determining step of the reaction is the epoxide ring closure. The activation energies predicted for this step increase with the electron withdrawing capacity of substituents in line with the observed negative slopes of Hammett-like relationships. The nucleophilic mechanism suggested by the present calculations does not conflict with observed stereospecificity of this reaction. Olefin substituents cause Hammond effects on the predicted transition structures, which are particularly pronounced on those geometrical parameters having the dominating contributions in the corresponding transition vectors. These predictions are in line with qualitative reaction surface models, but in contrast with VB considerations.

Olefin epoxidation by peroxyacids, or the Prilezhaev reaction, is an important reaction for structural studies and transformations due to the extreme simplicity of experimental conditions and high stereospecificity[1]. This reaction is also regiospecific in the majority of cases in terms of availability of options to oxidize the necessary double bonds in the presence of such with various reactivity[1]. Some exceptions to the latter are known[2] and these stimulated the interest to the present work. A variety of mechanisms (not less than five) has been suggested for this reaction[1] and most of these assume electrophilic addition of the oxidant to the olefinic bond. An alternative considers 1,3-dipolar cycloaddition[3]. Hammett type relationships for epoxidation of styrenes by peroxybenzoic acids have been considered as supporting an electrophilic mechanism[4]. The measured secondary deuterium kinetic isotope effects have also been interpreted in favour of electrophilic mechanism[5]. Moreover, kinetic studies[4,5]

have provided the background for the statement that the reaction involves an unsymmetrical transition structure as shown on the following Scheme:



A sufficiently reliable choice among the several existing alternative mechanisms suggested for the interaction between olefins and peroxyacids could be taken on the basis of quantum chemical calculations. The early experience in this respect, based on pi-electron calculations, has been rather discouraging[6]. More recent ab initio minimal basis calculations[7] have apparently substantiated the preference to unsymmetrical transition "states" and electrophilic mechanism, in line with the conclusions based on kinetical studies[4,5]. However, the term "transition state" has been used in this study "rather loosely"[8] and the structures obtained correspond actually to minima within the imposed geometry constraints. A more correct conclusion based on the mentioned calculations should probably state that the unsymmetrical approach of peroxiacid to olefin is energetically favoured[9]. Uncertainties about the interaction of peroxyacids and olefins arise also from the calculations of (isolated) peroxyacid molecules, which result in negative gross charges on all oxygen atoms[10]. These results are the source for the suggestion that this reaction is more likely orbital rather than charge controlled[10]. Thus, a detailed study of the potential surface for the interaction of peroxyacids and olefins might be expected to give further insight into the mechanism of this reaction provided that the stationary points found are rigorously characterised as minima, transition structures, or higher order saddle points[11].

Models and Methods of Calculation

The simplest model for the studied Prileshaev reaction is the interaction of peroxyformic acid and ethylene. The effects of substituents on the reaction profiles and transition structures are modelled for simplicity with substituted ethylenes. The smallest possible model among these consists of 6 non-hydrogen atoms, and the use of an adequate nonempirical level of calculations (e.g. 3-21G) for the detailed study of the potential energy surface would be rather unrealistic. For this reason semiempirical MNDO calculations[12] were used to scan the reaction paths. MNDO has proved sufficiently reliable in the studies of chemical reactivity[13,14] due to the relatively correct predictions of energy features and, in particular, to predictions of transition structures in good agreement with ab initio calculations[14]. MNDO, however, performs relatively poorly for molecules with adjacent electron pairs[15] and a reinvestigation of the predicted transition structures by 3-21G calculations[16] is now under way.

The calculations were carried out by the standard MNDO[17] and MOPAC[18] programs, as well as with MONSTERGAUSS[19] and HONDO-5[20]. All geometries were optimized without constraints and transition structures were identified by calculation of the corresponding force constant matrices under the requirement for a single negative eigenvalue, or a single imaginary vibrational frequency[11]. Preliminary searches for these structures were carried out by following the minimum energy reaction paths, MERP. The reaction coordinates used in the latter were the distance C...O and the valence angle O-C-C. The geometry

optimizations along MERP's were performed by the gradient method of Davidon, Fletcher and Powell[21] and the precise location of the transition structures by direct minimization of the energy gradients with respect to all geometrical parameters[22,11] of the reaction systems studied.

RESULTS AND DISCUSSION

If two neutral molecules of peroxyformic acid and ethylene are brought together, and the distance R_{oo} between the terminal oxygen and a carbon atom is used as the reaction coordinate, the resulting MERP is a rapidly rising curve for values of R_{oo} in the range 2.5 to 1.3 A. As the energy gradient along the reaction coordinate is increasing in absolute value in the same direction, no stationary point can be expected on the energy profile. Thus, present MNDO calculations do not confirm the earlier suggestion of an electrophilic attack of olefin by neutral peroxyacid molecule based on kinetical studies[4,5]. No support is given also to the same conclusion, based on minimal basis ab initio calculations of "transition state structures"[7].

The MERP of protonated peroxyformic acid and ethylene is a different curve. At 1.784 A it has a maximum, TS+, 39.1 kcal/mol (Table 1) higher than starting reactants, and at smaller values of the reaction coordinate R_{oo} the energy of the system drops rapidly. At the maximum of energy the calculated O-O distance is 1.435 A, while MNDO gives for HCOOOH 1.289 A, and for the protonated at the carbonyl oxygen $HCOOOH_2^+$ 1.302 A. As R_{oo} decreases, the O-O bond dissociates, while the newly formed valence angle OCC decreases from 100° to 60° - 55°, the value in the reaction product, oxirane. MNDO calculations indicate that electrophilic epoxidation of olefin by protonated peroxyacid is rather feasible and should proceed via the unsymmetrical transition structure TS+, similar to that postulated previously by Hanzlik and Shearer[5] and studied more recently by Plesnicar et al.[7] Its geometry, however, differs considerably from minimal basis set predictions[7]; note that the latter concern, most probably, local minima. The reaction coordinate is relatively completely represented by R_{oo} at distances larger than the value, corresponding to TS+. For the latter structure the dominating components of the transition vector are R_{oo}, which corresponds to the bond being formed, R_{oo}, which corresponds to the dissociation of O-O, and the angle CCO, which corresponds to the forthcoming ring closure.

Another feasible reaction path is the nucleophilic addition of peroxyformate anion to the olefinic double bond. In this case the calculated MERP increases smoothly for values of R_{oo} from 2.5 to 1.863 A. At the latter distance a transition structure occurs, TS1, Fig. 1, whose parameters are similar to those found in the case of nucleophilic addition of hydride to ethylene[23]. The calculated MNDO activation enthalpy is 22 kcal/mol. A relatively shallow minimum occurs at smaller values of the reaction coordinate. The structure, predicted by MNDO for this intermediate, corresponds to a "normal" product of nucleophilic addition, but with smaller negative charge at the free carbon atom than would have been expected for a carbanion, see Table 3. To follow the reaction further, a change of the reaction coordinate is required, and the valence angle CCO provides a relatively good description of the oxirane ring closure. Starting from 110° for the intermediate minimum, a new transition structure was found at $\angle CCO = 81.4°$, TS2, Fig. 2. The calculated activation enthalpy is 13.1 kcal/mol from the intermediate, or 27.7 kcal/mol from the initial reactants. While relatively small changes in R_{oo}, 1.497 to 1.401 A, and R_{oo}, 1.298 to 1.495 A, are calculated between the intermediate and TS2, after the latter R_{oo} drops to

ca. 1.3 A, a value smaller than calculated for oxirane, 1.417 A (MNDO), and formate anion is cleaved. The calculated activation enthalpy is considerably smaller than found for the electrophilic mechanism discussed above.

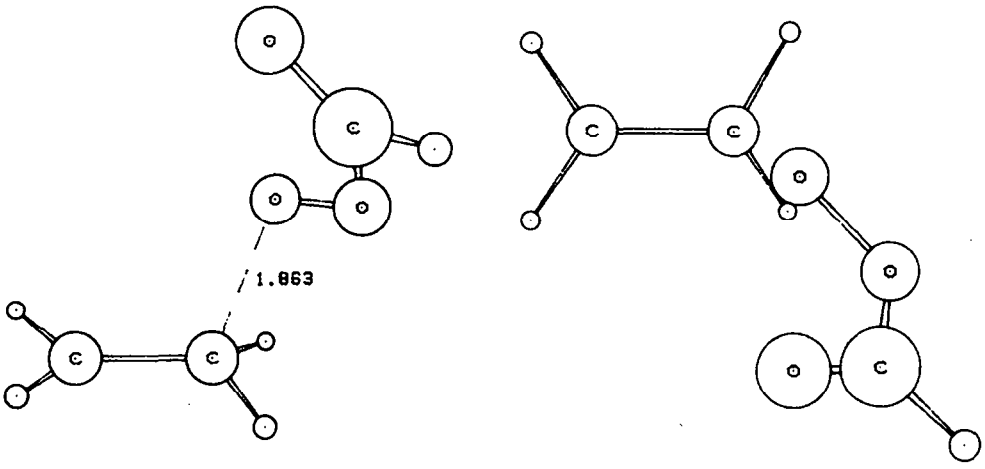


Fig. 1: Two projections of TS1, the transition structure for the nucleophilic addition of peroxyformate anion to ethylene

Similar considerations were applied to the interaction of acrolein and peroxyformic acid in its neutral, anionic, and protonated forms. These were intended to model the epoxidation of the conjugated double bond of artemisia ketone[2]. Neutral molecules of acrolein and peroxyformic acid give with respect to R_{CO} a MERP similar to the case with ethylene, with no indication for the existence of stationary points. The MERP for the electrophilic interaction of protonated on the carbonyl oxygen peroxyformic acid and acrolein, however, gives a maximum at R_{CO} = 1.70 A, TS+. This result is also similar to the case with ethylene except that the calculated activation enthalpy is considerably higher, 47.1 kcal/mol (Table 1). The nucleophilic interaction of peroxyformate anion and acrolein gives exothermically an adduct without activation energy. This adduct, along a MERP defined by the angular reaction coordinate ∠CCO, gives the final epoxide. The maximum of this MERP, a TS2, occurs at ∠CCO = 77.5°, and the calculated activation enthalpy is 30.6 kcal/mol from the stable adduct, or only 8 kcal/mol from the starting reactants. Thus, the present MNDO calculations reproduce correctly the lesser affinity of olefins with acceptor substituents to electrophilic epoxidation and, simultaneously, their greater affinity to nucleophilic epoxidation. The calculated very high activation enthalpy for epoxidation by protonated peroxyacid is in line with the absence of acid catalysis of the studied reaction[1,4]. The predicted preference of olefin epoxidation to nucleophilic mechanism, however, seems intuitively questionable, and a number of objections may be raised.

Negative slopes of Hammett-type extrathermodynamic relationships, in general, do not support a nucleophilic mechanism. The present MNDO calculation, however, predicts nucleophilic addition as the first, rapid reaction step. The second step is evidently electrophilic with respect to the olefin and the calculated activation enthalpies are larger, i. e. the rate determining step is actually predicted to be affected by olefin substituents in the experimentally observed direction. Another substantial objection is that a nucleophilic mechanism could not be stereospecific. In fact the epoxidation of α,β -unsaturated aldehydes or ketones by H_2O_2 in alkaline media is only stereoselective[1], as the

Michael type addition of HO_2^- gives actually a stable enolate anion. The cyclisation of the latter is relatively hindered and apparently slow enough for an internal rotation to occur. Other known epoxidation reactions in basic media are also interpreted in terms of complicated intermediates in order to avoid any assumption of nucleophilic addition and to explain stereospecificity[24]. However, this objection applies to any ionic mechanism and, therefore, the suggestion of Plesnicar[1] that the stereospecificity may be due to the relatively low activation energy, 16 - 18 kcal/mol[4] of the reaction, which could occur faster than an internal rotation is likely more acceptable. Indeed, the rotation would be sufficiently hindered even by small residual π-character of the former double bond in the intermediate carbanion[1b]. Present calculations support this suggestion showing stronger C-C bonding than for a single bond, Table 3.

Table 1: MNDO heats of formation and relative energies of species participating in the model Prileshaev reaction, kcal/mol.

Species	H_f	H_f	comments
C_2H_4	15.3		
C_2H_4O	-15.5		oxirane
HCOOH cis	-92.6		
$HCOO^-$	-101.7		
HCOOOH cis,cis	-65.8		
$HCOOO^-$	-66.9		
$C_2H_5O^+$	173.6		protonated oxirane
C_3H_4O	-18.1		trans-acrolein
$C_3H_5O^+$	153.4		protonated acrolein
$C_3H_4O_2$	-30.6		epoxy-propanal
$C_3H_5O_2^+$	154.5		protonated epoxypropanal
C_3H_6O	-27.5		methoxy-ethylene
$C_3H_6O_2$	-56.3		methoxy-oxirane
C_2H_3Cl	5.3		chloro-ethylene
C_2H_3ClO	-23.2		chloro-oxirane
C_3H_6	4.9		propene
C_3H_6O	-23.0		methyl-oxirane
$C_3H_5O_3^-$	-30.0	21.6	C_2H_4 + $HCOO^-$, TS1
$C_3H_5O_3^-$	-36.9	14.7	adduct
$C_3H_5O_3^-$	-23.6	28.0	C_2H_4 + $HCOO^-$, TS2
$C_3H_7O_3^+$	171.1	39.1	C_2H_4 + $HCOOH_2^+$, TS+
$C_3H_4ClO_3^-$	-64.7	-3.1	C_2H_3Cl + $HCOO^-$, adduct
$C_3H_4ClO_3^-$	-44.5	20.2	C_2H_3Cl + $HCOO^-$, TS2
$C_4H_5O_4^-$	-107.9	-22.9	acrolein + $HCOO^-$, adduct
$C_4H_5O_4^-$	-78.2	29.7	acrolein + $HCOO^-$, TS2
$C_4H_7O_4^-$	-78.4	16.0	$H_3COCH{=}CH_2$ + $HCOO^-$, TS1
$C_4H_7O_4^-$	-89.5	4.9	same as above, adduct
$C_4H_7O_4^-$	-78.4	16.0	same as above, TS2
$C_4H_7O_3^-$	-38.0	24.0	propene + $HCOO^-$, TS2

Another objection, that no intermediates have been observed[1e] could be countered by the argument that both experimental and calculated (usually overestimated) MNDO activation barriers to the exothermic olefin epoxidation are sufficiently low and the possible intermediates may well have been overlooked,

since the reaction has been used mostly for preparative purposes. It was felt, however, that additional calculations would be necessary to substantiate the counterarguments to the above objections. For this purpose the nucleophilic attack of peroxyformate anion was modelled on an olefin, substituted by an acceptor, Cl, and on an olefin, substituted by a donor, OCH_3. All calculated energies are collected in Table 1, and selected structural parameters of the predicted transition structures are listed in Table 2.

The calculated activation enthalpies for epoxidation by peroxyformate anion in the series of substituted ethylenes increase in line with increasing electron-withdrawing capacity of the substituents, 11.1 kcal/mol (CH_3O), 13.3 (H), 25.3 (Cl), and 29.7 (CH=O) for the rate determining step, Table 1. This result is in line also with the observed Hammett- type relationships between the rate constants and substituent constants[4]. Present MNDO calculations predict that stronger electron acceptors facilitate the exothermic formation of intermediate adducts without activation energy. In such cases the studied reaction is predicted to proceed via an one-step mechanism and to be sensitive to basic catalysis, which also agrees with the observed reactivity of this kind of substrates. The MNDO calculations for epoxidation of ethylene or methoxyethylene predict a relatively low activation barrier to the rapid formation of intermediates. The conversion of the latter into the corresponding oxiranes requires higher activation enthalpy and should be thus the rate determining step of the reaction. The overall activation energies are considerably lower than calculated for olefins with acceptor substituents. These results render support to the suggestion that the rapid oxirane ring closure is the reason for the stereospecificity, as well as to the assumption of two distinct steps of the studied reaction.

The relatively high exothermicity of the epoxidation reaction is an argument in favour of the suggestion that, in spite of the insignificant α-effect of $HCOOO^-$, estimated by 3-21G calculations[25] (0.4 kcal/mol relative to CH_3O^- or $HCOO^-$, i.e. $HCOOO^-$ is only ca. 2 times better as nucleophile, Table 4), olefins are capable of trapping the peroxyformate anion in non-polar solvents.

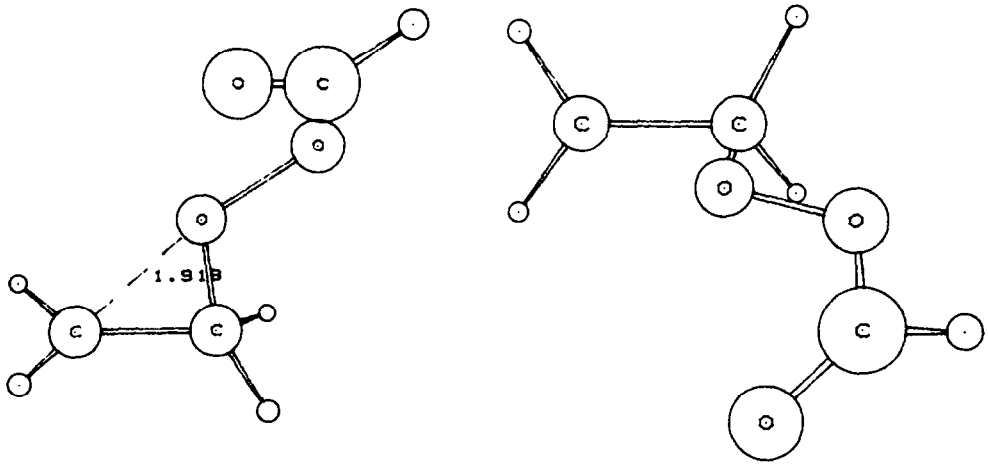


Fig. 2: Two projections of TS2, the transition structure for the oxirane ring closure.

The predicted structural parameters for TS1 and TS2 involving several olefin substituents provide an opportunity to check the validity of an important qualitative concept, the Hammond postulate[26]. As the calculated MNDO thermochemical effects for the formation of the intermediate adduct are positive, the

Hammond postulate requires for donor substituents (CH_3O) and unsubstituted ethylene transition structures more similar to that of the intermediate. Actually, TS1 structures are predicted only for the two mentioned cases. Since the formation of intermediate adducts of $HCOOO^-$ to chloroethylene and acrolein is predicted exothermic, the Hammond postulate would require reactant-like transition structures. It is quite conceivable that these structures might be so reactant-like that the largest used value of the reaction coordinate R_{co}, 2.5 A, is too small for their proper description. In addition, the validity of the MNDO model for such supermolecular distances is rather questionable.

Table 2: Calculated thermochemical effects (MNDO) of the nucleophilic Prileshaev reaction, and selected structural parameters of predicted stationary points on the energy surface, kcal/mol, angstroms, and degrees.

A: Nucleophilic addition of $HCOOO^-$ to olefins, TS1

Substituent	$\Delta\Delta H_f$	R_{co}
-CHO	-22.9	?
-Cl	-3.1	?
$-OCH_3$	4.9	1.915
-H	14.7	1.863

B: Structural parameters of intermediate adducts

Substituent	R_{c1o1}	R_{c2o1}	R_{o1o2}	$<C_1C_2O_1$	R_{c1c2}
-CHO	1.4546	2.3822	1.2979	113.95	1.4695
-Cl	1.4821	2.5063	1.2859	118.63	1.4321
$-OCH_3$	1.4795	2.3887	1.2981	109.51	1.4453
-H	1.4982	2.3874	1.2980	116.67	1.4223

C: Cyclization of intermediates to oxiranes, TS2

Substituent	$\Delta\Delta H_f$	R_{c1o1}	R_{o1o2}	R_{c2o1}	$<C_1C_2O_1$	$\Delta\Delta H_f$, total
-CHO	-24.7	1.3892	1.5564	1.7972	77.5	-47.3
$-CH_3$		1.3951	1.5141	1.8821	82.3	-62.7
-Cl	-60.5	1.4014	1.5020	1.8419	80.3	-63.6
$-OCH_3$	-69.8	1.3974	1.5042	1.8882	82.5	-64.4
-H	-80.3	1.4024	1.4882	1.9177	84.5	-65.6

The transition structures TS2 for the second step of the nucleophilic epoxidation are of greater interest in this respect. As the calculated MNDO thermochemical effects for this step are negative, the Hammond postulate requires that all TS2 are reactant, i.e. intermediate-like. The less exothermic the predicted cyclisation to oxirane, the more similar is the particular TS2 to the final product. Hammond effects are manifested in all structural parameters contributing significantly to the corresponding transition vectors, namely, the

bond making $R_{c_2o_1}$, the bond breaking $R_{o_1o_2}$, and the ring closure angle COO, see Table 2.C. Closer examination of the latter shows that in the case of chlorine as substituent some disobeyance to the Hammond rule might indicate more subtle effects on the transition structure.

Table 3: MNDO charges and bond orders at some stationary poins of the reaction surfaces.

A: Intermediate adducts: charges and orders of the bonds to be formed and broken.

Substituent	C_1	C_2	O_1	O_2	C_2O_1	O_1O_2	C_1C_2
-CHO	0.2876	-0.5957	-0.1906	-0.1915	0.0397	0.9498	1.0399
-Cl	0.3188	-0.6220	-0.2655	-0.1526	0.0775	0.9653	1.1381
$-OCH_3$	0.3069	-0.5806	-0.2418	-0.1868	0.0928	0.9321	1.1273
-H	0.3156	-0.6840	-0.2697	-0.1860	0.1188	0.9243	1.2288

B: Transition structure TS2: charges and orders of the bonds being formed and broken.

Substituent	C_1	C_2	O_1	O_2	C_2O_1	O_1O_2
-CHO	0.2051	-0.4417	-0.0629	-0.4341	0.4442	0.4543
$-CH_3$	0.2330	-0.5092	-0.1037	-0.4054	0.4346	0.4955
-Cl	0.2182	-0.3631	-0.0909	-0.4016	0.4388	0.5105
$-OCH_3$	0.2287	-0.3643	-0.1215	-0.3975	0.4211	0.5059
-H	0.2301	-0.4922	-0.1338	-0.3872	0.4268	0.5240

The calculated electronic indices for the transition structures TS2 show similar "Hammond trends". It is of interest to compare the present MNDO results with the predictions of qualitative reaction surface models[27]. If the cyclization of the intermediate adducts to oxiranes is regarded as a S_N2 substitution over the terminal oxygen atom of (the former) peroxyformate, these models predict that the better the nucleophile, the more advanced would be the bond breaking with the leaving group, and little effect on the bond making between the nucleophile and the reaction center. Present MNDO calculations confirm the first part of this prediction, but show also comparable Hammond effects on the bond making. In contrast, valence bond considerations[28] predict anti-Hammond effects of changes in the nucleophile for this type of reactions.

The calculated MNDO thermochemical effects of the overall reaction of ethylene with protonated $HCO_3H_2^+$ and neutral peroxyformic acid HCO_3H, and peroxyformate anion $HCOOO^-$ are -51, -57.6, and -65.6 kcal/mol, respectively, Table 1. 3-21G calculations, however, give for HCO_3H and C_2H_4 an effect of -33.3 kcal/mol, and for $HCOOO^-$ and C_2H_4 an effect of-31.3 kcal/mol, Table 4. In addition, 3-21G energies of TS1 and TS2, at the MNDO geometries, are 50.3 and 60.2 kcal/mol higher than the starting reactants. These results indicate that the stationary points on the 3-21G energy surface may correspond to structures significantly different from MNDO ones. It is thus evident that MNDO calculations do not say the final word of the theory about the mechanism of the

Prilezhaev reaction.

Table 4: Ab initio 3-21G energies, used in the thermochemical evaluations (in atomic units; 1 a.u. = 627.5 kcal/mol) and affinities of nucleophiles to proton (PA) and methyl cation (CA, in kcal/mol).

	E, total	PA, calc	PA, exp	CA, calc	CA, exp
CH_3O^-	-113.72190	424.3	379.2	302.6	267.6
$HCOO^-$	-187.10463	373.7	345.2	251.3	233.1
$HCOOO^-$	-261.45447	371.7		249.0	
CH_3OH	-114.39802*				
HCOOH	-187.70019*				
HCOOOH	-262.04681*				
CH_3OCH_3	-153.21321*				
$HCOOCH_3$	-226.51427*				
$HCOOOCH_3$	-300.86041				
CH_3^+	-39.00913				
C_2H_4	-77.60099*				
HCOOOH[a]	-262.04668*				
C_2H_4O	-152.00070*				
HCOOH[a]	-187.68868*				
TS1**	-338.97545				
TS2**	-338.95955				

a) trans- isomers
*) ref. 29
**) calculated at the MNDO geometry

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