

KINETICS OF REACTIONS OF PROTOTYPICAL AROMATIC HYDROCARBONS
WITH O (³P) ATOMS AND CH₂ (\bar{X} ³B₁) RADICALS: A COMPARATIVE STUDY

F. Temps and H. Gg. Wagner
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10,
3400 Göttingen, Germany

Keywords: Aromatics, kinetics, methylene radicals, oxygen atoms.

INTRODUCTION

Mono- and polycyclic aromatic hydrocarbons constitute important intermediates and by-products of technical combustion processes (see, e.g., [1]). Their build-up and subsequent fate is well appreciated to be critically determined by reactions with small, highly reactive O- or C-containing radicals. However, despite their importance, the detailed mechanisms and kinetics of the distinctive elementary reactions which can take place still present many questions. In the present paper we consider reactions of selected aromatic hydrocarbons with two particularly interesting free radicals, namely O (³P) (\equiv ³O) and CH₂ (\bar{X} ³B₁) (\equiv ³CH₂). While O is an important oxidizing species, CH₂ as the most abundant highly reactive C-centered small radical in flames can contribute to the build-up of larger molecules by adding reactive side groups to a substrate. Recent experimental results for the kinetics of both species with prototypical unsubstituted mono- and polycyclic aromatics as well as simple alkyl substituted derivatives are summarized. Reactants include benzene, naphthalene, phenanthrene, toluene, ethylbenzene, and cumene. The investigations were motivated by the desire to find some simple correlations which would help to estimate rate parameters for ³O or ³CH₂ with other reactants for which experiments cannot be performed easily. Thus, the focus is on a critical comparison of the chemical reactivities of the two radicals, which since they are isoelectronic are expected to exhibit parallel reactivities. Analogies have been observed concerning addition reactions to the aromatics. On the other hand, H atom abstraction from alkyl side chains could only be observed for ³CH₂ but seems to play little role for ³O. A difference with dramatic importance to combustion processes arises as a consequence of the low singlet-triplet splitting between CH₂ (\bar{X}) and CH₂ (\bar{a} ¹A₁) (\equiv ¹CH₂), $\Delta H_0^\ddagger = 37.7$ kJ/mol [2].

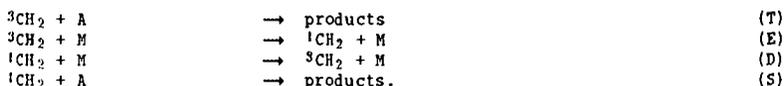
EXPERIMENTAL

Experimental studies of reactions of ³O and ³CH₂ with aromatics A have been performed using the discharge flow technique. Experimental set-ups have been described [3a, 4]. Reactions of ³O atoms were studied in the temperature range 300 K \leq T \leq 880 K under pseudo-first-order conditions with [O] \gg [A]. Absolute O concentrations were determined using the titration reaction N + NO. Concentration-versus-time profiles of O and A were followed by mass spectrometry. The reactions of ³O with benzene and toluene were also investigated using the shock tube technique [3e-f]. Reactions of ³CH₂ were studied in the temperature range 360 K \leq T \leq 700 K under conditions [A] \gg [³CH₂] with Laser Magnetic Resonance (LMR) detection of ³CH₂. The reaction O + CH₂CO \rightarrow CH₂ + CO₂ served as the radical source. Reaction product were determined by GC or GC-MS analysis after photolyzing CH₂CO at either $\lambda_1=366$ or $\lambda_2=312$ nm in a static cell in the presence of reactants A [5a]. CH₂CO photodissociation at these wavelengths yields practically only ³CH₂ or ¹CH₂, respectively [6].

RESULTS AND DISCUSSION

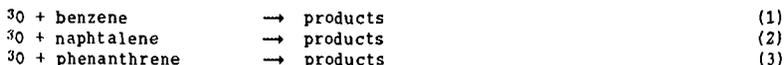
The rate coefficients for the reactions of ^3O with reactants A can be determined directly from the pseudo-first-order decay plots of [A] and the known O concentrations. Performing experiments under the condition $[\text{O}] \gg [\text{A}]$ has the advantage that heterogeneous processes and consecutive reactions of the various products can hardly affect the kinetic results. ^1O atoms play no role in thermal systems.

Data analysis for the reactions of $^3\text{CH}_2$ is somewhat more involved. Rate constants obtained from pseudo-first-order decay plots of $[\text{CH}_2]$ in the absence and presence of a large excess of [A] refer to the total depletion of $^3\text{CH}_2$ via all possible pathways [7]. In the first place one has the reactive channels (T) of $^3\text{CH}_2$ with the substrates. However, because of the small singlet-triplet splitting, partial thermal equilibration (E/D) with collision partners M between the two CH_2 electronic states has to be taken into account as well. $^1\text{CH}_2$ undergoes very fast consecutive reactions (S) with the reactants:



With the steady state assumption for $^1\text{CH}_2$, the rate coefficients for deactivation and reaction of $^1\text{CH}_2$ taken from independent measurements [8] and the rate for $^3\text{CH}_2$ excitation from the equilibrium constant for $^3\text{CH}_2 \rightleftharpoons ^1\text{CH}_2$, the experimental, directly measured effective rate constants can be separated to determine the rate coefficients for the $^3\text{CH}_2$ reactive channels (T) [5d, 7].

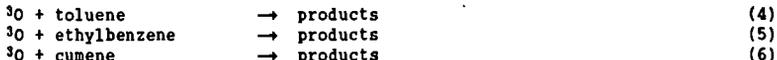
REACTIONS OF ^3O WITH UNSUBSTITUTED AROMATICS: The rate constants for the reactions of ^3O with the mono- and polycyclic unsubstituted aromatic hydrocarbons



are shown as a function of temperature in Fig. 1. Data points are from [3a-e]. Results for reaction (1) obtained in other laboratories (for references see [3a]) are in good agreement. Table 1 summarizes the Arrhenius parameters. The reactions can be seen to exhibit moderate activation energies. In accordance with theoretical expectations [9] benzene is the least reactive molecule. Naphtalene and phenanthrene behave very similarly. It is pointed out that the data for reactions (1) - (3) are in line with results for related molecules such as halogenbenzenes and pyridine [3i-j], which are less reactive than benzene, and biphenyl [3d], which reacts somewhat faster. Furthermore, in view of the different electron configurations the reaction with anthracene is expected to be significantly faster than the one with phenanthrene.

The reactions of ^3O with these aromatics proceed via addition to the ring systems yielding a triplet biradical as primary product. However, intersystem crossing to the singlet state is likely to be fast, and different isomerization and fragmentation reactions can also take place. The most exothermic reaction channels are those leading to phenols, which at high pressures can be collisionally stabilized. Formation of a seven-membered ring containing the O atom or of corresponding "epoxy" isomers are other possibilities. In the low pressure regime H elimination to yield phenoxy type radicals has been observed, while elimination of CO has been concluded to be of minor importance [10a]. H atom abstraction by ^3O from the aromatic ring is endothermic and has a high activation energy. Its role under flame conditions can be estimated from an Evans-Polanyi plot.

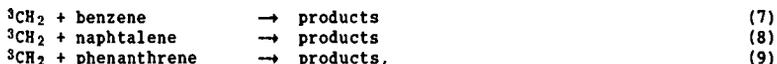
REACTIONS OF ^3O WITH ALKYL SUBSTITUTED AROMATICS: Compared to the unsubstituted aromatics discussed above, alkyl substituted derivatives stand out for their two reactive centers, the aromatic ring and the side chain. The measured activation energies and preexponential factors for the selected reactions



are given in Table 1. Experiments have been described in some detail in [3a, f, h]. Reaction (4) has also been studied in several laboratories (for references see [3a]), the different results being in good agreement with each other. The overall rate constants $k_4(T) - k_6(T)$ and, for comparison, $k_1(T)$ are plotted in Figure 2. Considering the overall body of data it is apparent that the kinetics of the reactions of ^3O with benzene derivatives containing a single alkyl group are virtually identical under the conditions used. The reactions are somewhat faster than with benzene. However, there is little if any dependence on the nature of the alkyl chain (methyl vs. ethyl vs. isopropyl). Data for xylenes [3h] indicate that a second alkyl substituent leads to some further acceleration of the reaction.

Concerning the reaction mechanism, the question arises whether the main reaction channels involve attack by ^3O of the aromatic ring or of the alkyl group. Because of the weak benzylic C-H bonds (e.g., $\Delta H_{298}[\text{H}-\text{CH}_2\text{C}_6\text{H}_5] = 378 \text{ kJ/mol}$ [11]) H atom abstraction from these sites is exothermic. An Evans-Polanyi plot for reactions of ^3O with alkanes extrapolates to a very low value for the activation energy of H abstraction from toluene of $\approx 10 \text{ kJ/mol}$. Accordingly, H abstraction might be expected to constitute a main channel. In contrast, in a shock tube investigation of reaction (4) the OH channel has been determined to account for only 10% at $T \approx 1100 - 1350 \text{ K}$. In a crossed molecular beam study of reaction (4) the addition-elimination products $\text{CH}_3 + \text{phenoxy}$ and $\text{H} + \text{cresoxy}$ were observed [10b]. Note also that the similarity of reactivities of toluene, ethylbenzene, and cumene despite of the significantly distinct benzylic C-H bond energies can be taken as evidence against H abstraction. However, an unambiguous answer cannot yet be given. Further experimental work is underway [12].

REACTIONS OF $^3\text{CH}_2$ WITH UNSUBSTITUTED AROMATICS: The rate parameters for the corresponding reactions of $^3\text{CH}_2$,

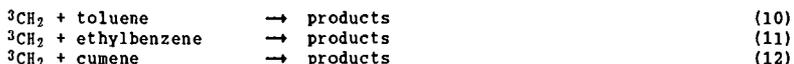


are listed in Table 1 [5b, e]. The different data points obtained from the LMR measurements and, for benzene, from an analysis of stable end products at room temperature are plotted in Arrhenius form in Fig. 1. Corrections for contributions from excitation to the singlet state and consecutive $^1\text{CH}_2$ reactions were applied as described [7]. In comparison to ^3O , $^3\text{CH}_2$ can be seen to be significantly less reactive. In particular, the reaction of $^3\text{CH}_2$ with benzene (7) exhibits almost twice as high an activation energy, its value being virtually equal to the CH_2 singlet-triplet splitting. Reactions (8) and (9) can be seen to be faster than (8), similar to the observations for ^3O , but still slower than $^3\text{O} + \text{benzene}$.

Fig. 3 shows product histograms for $^3\text{CH}_2$ as well as $^1\text{CH}_2 + \text{benzene}$ [5a]. $^3\text{CH}_2$ reacts via addition to the ring system. The product distributions under different conditions, including flame temperatures, can be rationalized with the help of unimolecular rate theory and the energy diagram of Fig. 4. At room temperature and pressures above a few mbars the reaction is in its high pressure limit

and cycloheptatriene is the main product. H abstraction by $^3\text{CH}_2$ from the aromatic ring would have an activation energy far above the singlet-triplet separation and thus cannot play a role in practical systems. The observed small yield of toluene (see Fig. 3) is an unambiguous manifestation of the partial thermal equilibration between $^3\text{CH}_2$ and $^1\text{CH}_2$ taking place even at room temperature. $^1\text{CH}_2$ reacts with benzene either via addition to the aromatic ring, giving cycloheptatriene as primary product, or via insertion into a C-H bond to yield toluene. Reaction products of naphthalene and phenanthrene can be rationalized by analogy.

REACTIONS OF $^3\text{CH}_2$ WITH ALKYL SUBSTITUTED AROMATICS: The results for reactions of $^3\text{CH}_2$ with a series of alkylbenzenes,



are given in Table 1 and illustrated in Fig. 2 [5c, d]. Reaction (11) has been discussed in some detail before [5d]. However, with the data for the related molecules the overall picture becomes apparent. The reactions of $^3\text{CH}_2$ with alkylbenzenes have much higher activation energies than what has been measured for ^3O . A most striking difference is the observation from Fig. 2 that the rate coefficients for (10) - (12) cannot be represented by single Arrhenius expressions. Instead, one has to distinguish two regimes. At high temperatures (> 450 K) the different alkylbenzenes exhibit virtually identical kinetics, regardless of the nature of the side group. "High temperature" activation energies for all three molecules are close to the one for benzene, suggesting addition of the $^3\text{CH}_2$ to the ring to account for the reaction. Similar behaviour has also been observed for p-xylene [5c]. Product yields can be predicted using unimolecular rate theory [5d]. At temperatures below 450 K reaction channels with much lower activation energies and lower preexponential factors play a role, and the kinetics of toluene, ethylbenzene, and cumene become distinct. Measured product distributions (see Fig. 3, [5a]) for reactions (10) and (12) indicate the importance of H abstraction from the alkyl groups of these molecules under these conditions. The observed high yields of ethylbenzene from (10) or n-propylbenzene and cumene from (11) are produced via the subsequent cross recombination of the primary products CH_3 and the respective "benzyl" radicals, e.g.



The combination of addition and abstraction channels produces the apparent curvature in the Arrhenius plots.

DISCUSSION: The general observation has been that $^3\text{CH}_2$ is a much less reactive species than ^3O . However, interesting common trends as well as some differences can be observed which shall be pointed out in the following.

From a study of H abstraction reactions from saturated hydrocarbons [7] the reactivities of $^3\text{CH}_2$ are to vary with reactants in a manner parallel to the better known trends for ^3O . Fig. 5 shows the respective correlation. The differences in the activation energies for both species are of the order of only 5 kJ/mol. However, the bond strength is higher in the product H- CH_2 than in H-O (461 kJ/mol vs. 428 kJ/mol). The preexponential factors for reactions of $^3\text{CH}_2$ had been found to be lower by roughly an order of magnitude than for ^3O , reflecting the steric requirements to form the transition states [7].

The reactions of ^3O and $^3\text{CH}_2$ with the aromatic hydrocarbons, as with other unsaturated reactants, are dominated by the electrophilic character of the radicals.

The correlations between activation energies for corresponding reactions are shown in Fig. 5. Different families of reactants (alkenes vs. alkyne vs. unsubstituted aromatics vs. alkylaromatics) exhibit different trends. For 3O the activation energies are known to correlate with the ionization potentials of the reactants [13, 3d]. Analogous trends can be observed for 3CH_2 . Some theoretical support for such a correlation stems from recent ab initio quantum chemical computations of the potential energy surface for the reaction of 3CH_2 with C_2H_4 by Peyerimhoff and coworkers [14], who found the critical phase of the reaction to be accompanied by a charge transfer from the C_2H_4 moiety towards the methylene C. Loosely speaking, the energetics of the transition state regions might thus be expected to depend on the ease of charge transfer from the reactant, for which the ionization potential is a rough measure. Other factors, however, play a role as well. For instance, the activation energies for reaction of 3CH_2 with tetramethylethylene and cycloheptatriene have been observed to be much higher than expected from the simple correlations [5e]. For the first molecule hindrance by the methyl groups must be considered, whereas for the latter electronic effects due to the three conjugated π -bonds can play a role.

The preexponential factors for the addition reactions of 3O and 3CH_2 to aromatics differ little. It is noted, however, that the 3CH_2 values depend on the correction for the pathway via excitation of 3CH_2 to the singlet state. Thus, they contain somewhat higher systematic uncertainties than the activation energies. In view of the spectroscopically known singlet-triplet couplings in CH_2 , it is an interesting speculation, whether the chemical differences between " 1CH_2 " and " 3CH_2 " decrease towards high temperatures (high internal excitation). 1CH_2 is known to react with hydrocarbons with close to unit collision efficiency [8]. At room temperature, the observed distinct products of CH_2 in the two spin configurations indicate that both species do react independently. This picture is substantiated by the ab initio potential surface of Peyerimhoff [14], who showed the minimum energy pathways for the approach of CH_2 in both spin states to C_2H_4 to be entirely different, leaving little room for singlet-triplet conversion during the reaction. Instead, CH_2 singlet-triplet intersystem crossing seems to be governed by long-range processes [8, 15]. Little is known, however, about the reaction dynamics of 3CH_2 in vibrationally excited states, which would certainly be of importance under the conditions of combustion processes. In any case, for modeling combustion processes the distinct chemistry of 1CH_2 , which has been well established now [8] but which cannot be discussed here in more detail has to be taken into account.

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TABLE 1: Arrhenius parameters for reactions of ^3O and $^3\text{CH}_2$ with aromatics.

Reaction	A [$\text{cm}^3/\text{mol}\cdot\text{s}$]	E_a [kJ/mol]
^3O + benzene	$2.4 \cdot 10^{13}$	19.5
^3O + naphtalene	$1.4 \cdot 10^{13}$	7.5
^3O + phenanthrene	$1.9 \cdot 10^{13}$	7.7
^3O + toluene ^{a)}	$2.2 \cdot 10^{13}$	15.6
^3O + ethylbenzene ^{a)}	$2.2 \cdot 10^{13}$	15.9
^3O + cumene ^{a)}	$2.0 \cdot 10^{13}$	15.3
$^3\text{CH}_2$ + benzene	$3.0 \cdot 10^{13}$	37.9
$^3\text{CH}_2$ + naphtalene	$1.3 \cdot 10^{13}$	27.9
$^3\text{CH}_2$ + phenanthrene	$2.2 \cdot 10^{13}$	28.3
$^3\text{CH}_2$ + toluene ^{b)}	$6.0 \cdot 10^{13}$	36.8
$^3\text{CH}_2$ + toluene ^{c)}	$2.0 \cdot 10^{11}$	19.0
$^3\text{CH}_2$ + ethylbenzene ^{b)}	$6.0 \cdot 10^{13}$	36.8
$^3\text{CH}_2$ + ethylbenzene ^{c)}	$1.6 \cdot 10^{11}$	13.6
$^3\text{CH}_2$ + cumene ^{b)}	$6.0 \cdot 10^{13}$	36.8
$^3\text{CH}_2$ + cumene ^{c)}	$3.0 \cdot 10^{11}$	13.6

a) Presumably addition reaction, see text.

b) Addition reaction to aromatic ring, see text.

c) Estimated values, H atom abstraction from alkyl group, see text.

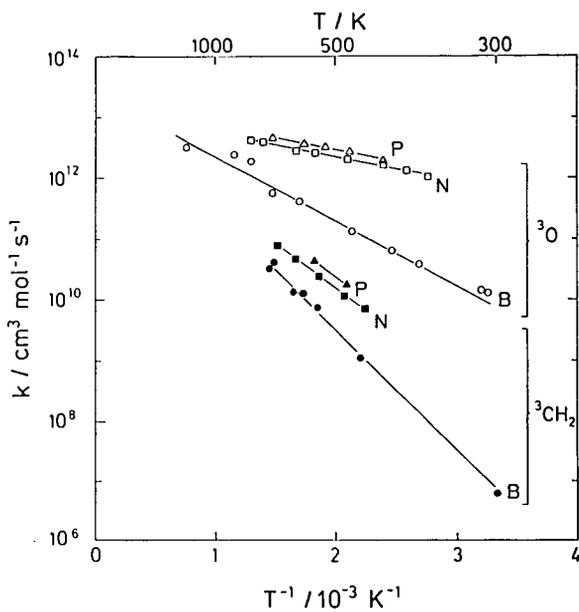


FIGURE 1: Arrhenius plot for the reactions of ^3O and $^3\text{CH}_2$ with benzene (B), naphthalene (N), and phenanthrene (P).

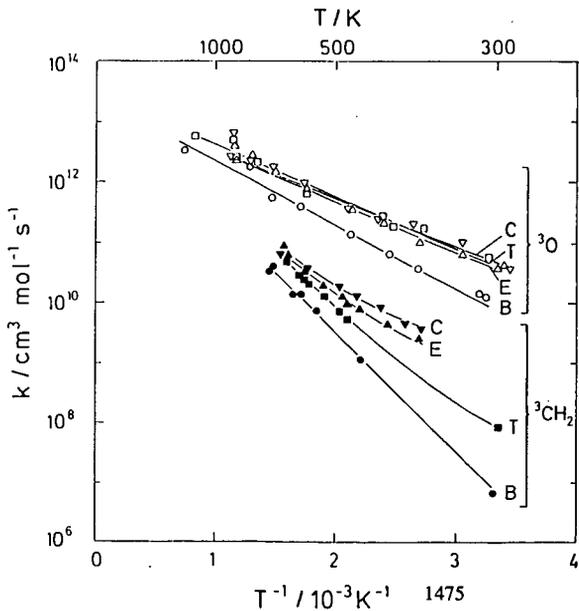


FIGURE 2: Arrhenius plot for the reactions of ^3O and $^3\text{CH}_2$ with benzene (B), toluene (T), ethylbenzene (E), and cumene (C).

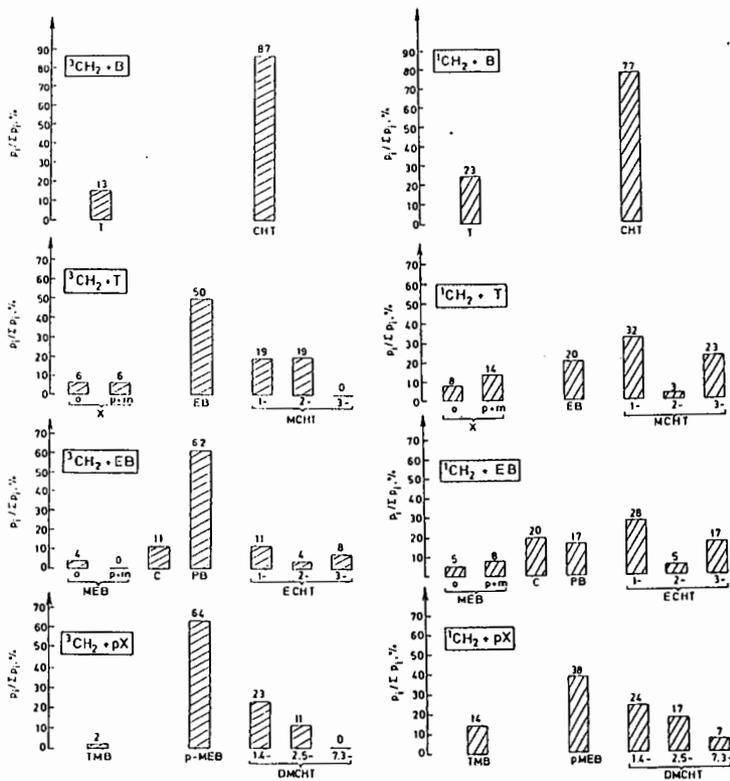


FIGURE 3: End product distributions for the reactions of $^3\text{CH}_2$ and $^1\text{CH}_2$ with benzene, toluene, ethylbenzene, and p-xylene [5a]. B = benzene, T = toluene, CHT = cycloheptatriene, X = xylene, EB = ethylbenzene, MCHT = methylcycloheptatriene, MEB = methylethylbenzene, C = cumene, PB = n-propylbenzene, ECHT = ethylcycloheptatriene, TMB = trimethylbenzene, MEB = methylethylbenzene, DMCHT = dimethylcycloheptatriene.

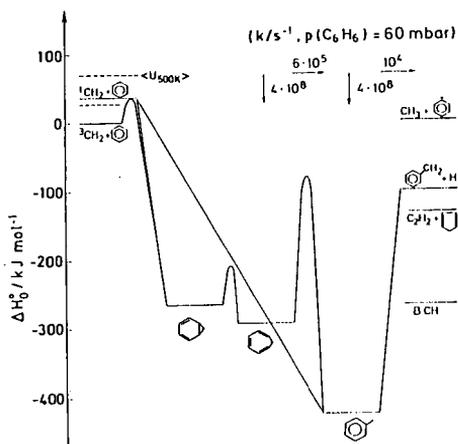


FIGURE 4: Energy diagram for the reactions of ³CH₂ and ¹CH₂ with benzene [5b].

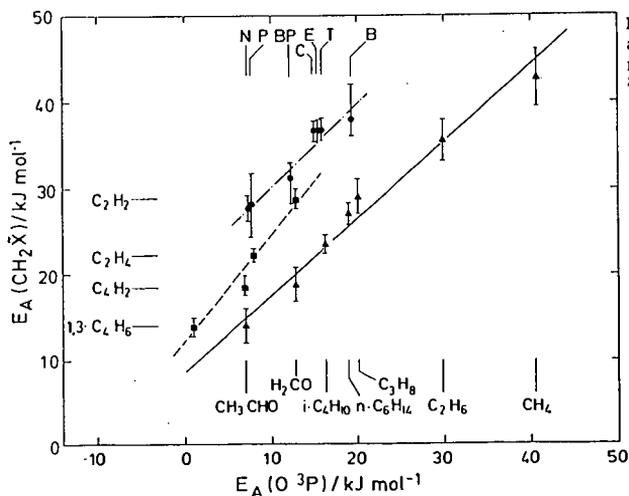


FIGURE 5: Correlation of activation energies for reactions of ³O and ³CH₂.