August, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 54, 2439—2443 (1981)* 2439

UV Absorption Studies of the Pyrolysis of Butane in Shock Waves

Tohru Koike* and Kihei Morinaga
Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239

(Received December 19, 1980)

The UV absorption measurements at 216 nm were carried out for three shock-heated mixtures, 1, 2, and 2.8% n-C_4H_{10} diluted in Ar, in the temperature range of 1290—1610 K and at about half atmospheric pressures. From the initial absorption rise, which can be attributed to the CH_3 growth, the rate constant of the reaction, n-$C_4H_{10}=CH_3+n$-C_3H_7, was evaluated as $k_2=8.9\times10^{13}\exp(-71.9\ \mathrm{kcal}/RT)$ (s^{-1}). A computer modeling using a 44-reaction mechanism including the k_2 value so evaluated could reproduce the absorption early in the reaction and in the temperature range of 1420—1610 K with a reasonable value.

The pyrolysis of butane has mainly been studied at lower temperatures using a flow tube[1-3] and a wall-less reactor.[4] The basic idea for the pyrolysis at low temperatures is almost established, and the features of the reaction are explainable through a free-radical mechanism of the Rice-Herzfeld type.[3,4]

At high temperatures, however, only a few studies of the pyrolysis have been reported.[5-7] Recently, shock-tube studies using TOF mass spectroscopy for the pyrolysis have been carried out and the observed concentration profiles of several species have been subjected to a computer modeling.[7] The results of the computer modeling at high temperatures were not as satisfactory as those in the low temperature region where the modeling results tolerably concurred with the observed profiles.[8,9]

The pyrolysis of n-C_4H_{10} has two channels for the initiation reaction:

$$n\text{-}C_4H_{10} = 2C_2H_5, \qquad (1)$$

$$n\text{-}C_4H_{10} = CH_3 + n\text{-}C_3H_7. \qquad (2)$$

Because of the fall-off effect, the rate constants of these unimolecular reactions at high temperatures may not accord with the values obtained by extrapolations of the rate constants at low temperatures. Therefore, it is desirable to measure the k values directly; this may be one of the most important steps in clarifying the reaction mechanism of the n-C_4H_{10} pyrolysis at high temperatures.

Recently, the absorption measurement at 216 nm of the CH_3 profile has been proved to be a useful method for studying the alkane pyrolysis. However, the measurement has thus far been applied only to the CH_4 and C_2H_6 pyrolysis[10] and the CH_3 recombination.[11]

In this study, we will estimate the k value of Reaction (2) by measuring the absorption profile at 216 nm in the n-C_4H_{10} pyrolysis. The k_2 value thus obtained is incorporated into a reaction mechanism of the pyrolysis, and the absorption profile at the early stage of the reaction is elucidated by computer modeling.

Experimental

The shock tube and the optical system used in this study have been described in a preceding paper.[12] The D_2-lamp of 30 W used before was replaced by a 200 W high-power one (Hanau, D200F) so as to gain much larger signals.

The gases used were 99.8% pure n-C_4H_{10} purchased from the Takachiho Co. and 99.999% pure Ar from the Nippon Sanso Co. The test gas compositions, n-C_4H_{10}/Ar, were 1/99, 2/98, and 2.8/97.2, while the starting pressure of the test gas was always 20 Torr (1 Torr=133.322 Pa). It was confirmed that no emission from the shocked test gas was observed.

The computer modeling for the observed absorption profiles was done using the flow model of the laminar-boundary-layer growth with limiting separation.[13]

Results and Discussion

A sample oscillogram of 216 nm light attenuation through the shocked gas is shown in Fig. 1. This oscillogram is a typical one for the present studies; *i.e.*, the absorption increases gradually right after the shock arrival at the observation window. Since no absorption has been reported for CH_4 and C_2H_6 at 216 nm,[14] n-C_4H_{10} was also expected to have no absorption band in this wavelength region.

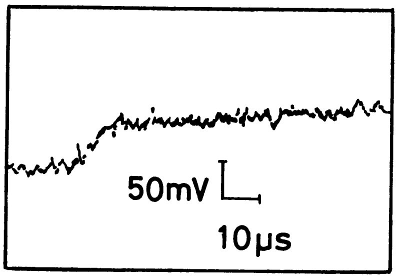

Fig. 1. A representative oscillogram for 2% n-C_4H_{10} in Ar mixture, P_1=20 Torr, and T_2=1436 K.

The absorption measurement of C_2H_5 in this wavelength range has been reported;[15] the absorptivity at 216 nm is at least 30 times smaller than that of CH_3. The effect of n-C_3H_7 on the measured absorption was assumed to be negligibly small. The validity of this assumption will be confirmed below by a computer modeling; the steady [n-C_3H_7] modeled is about 4 orders of magnitude less than the [CH_3]. Therefore, it is reasonable to assume that the absorption early in the reaction is entirely due to CH_3.

The primary reactions of the CH_3 radical at the early stage of the reaction are:

$$CH_3 + n\text{-}C_4H_{10} = CH_4 + n\text{-}C_4H_9, \qquad (5)$$

$$= CH_4 + s\text{-}C_4H_9, \qquad (6)$$

$$s\text{-}C_4H_9 = CH_3 + C_3H_6, \qquad (11)$$

$$n\text{-}C_3H_7 = CH_3 + C_2H_4. \qquad (24)$$

The methyl radical produced by Reaction 2 decreases as a result of metathetical reactions (5) and (6). The unimolecular decompositions of the radicals thus produced, Reactions 11 and 24, also give CH_3. At a very early time in the reaction, for example, lab. time of 0.2 μs, only Reactions 2 and 24 are important for evaluating the CH_3 profile; this can be confirmed by comparing the value of the rate of each reaction obtained by the computer modeling to be discussed later. The steady state assumption for $n\text{-}C_3H_7$ leads to the following expression of CH_3 production:

$$k_2 = (d[CH_3]/dt)_{t\to 0}/(2[n\text{-}C_4H_{10}]_0)$$

where t=particle time and $[n\text{-}C_4H_{10}]_0$ is the shock-front concentration of $n\text{-}C_4H_{10}$. To evaluate the k_2 value using the above equation, it is necessary to estimate the absorptivity of CH_3, which correlates the measured absorption to $[CH_3]$. We adopted the absorptivities reported by Tsuboi[10] and Glänzer *et al.*[11]

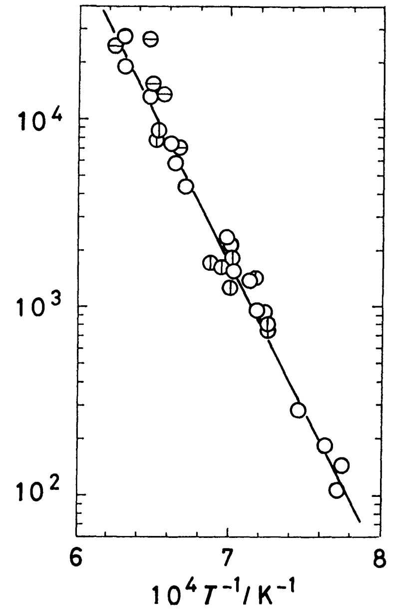

Fig. 2. Arrhenius plots for k_2. The symbols used are as follows.
⊖: For 1% $n\text{-}C_4H_{10}$ in Ar, ⦶: for 2% $n\text{-}C_4H_{10}$ in Ar, and ○: for 2.8% $n\text{-}C_4H_{10}$ in Ar.
The line shows a least squares fitting for the data points.

The k_2 values thus obtained are shown *vs.* $10^4/T$ in Fig. 2. A least-squares calculation for the relation provided the following Arrhenius expression:

$$k_2 = 8.9\times 10^{13}\exp(-71.9\ \text{kcal}/RT)\quad (\text{s}^{-1}).$$
$$(1\ \text{kcal} = 4.184\ \text{kJ})$$

The rate constants of the metathetical reactions are reported to show deviations from the Arrhenius plots, and the actual values of the rate constants at high temperatures are larger than those extrapolated from the k values measured at low temperatures.[2] It is also well known that the k value of the metathetical reaction decreases with an increase in the structual complexity of the radicals accompanying the reaction.[3] At an early time in the $n\text{-}C_4H_{10}$ pyrolysis, [H] is much smaller than $[CH_3]$ and $[C_2H_5]$. Therefore, it is expected that the value of k[R], where k and [R] are the rate constant and the concentration of the radical in the metathetical reaction respectively, will change depending on both the temperature and the reaction time. As for the unimolecular decompositions of the radical, the rate constant may be in the fall-off range under the present experimental conditions.

To elucidate the roles of these metathetical reactions and unimolecular decompositions of the radicals in the $n\text{-}C_4H_{10}$ pyrolysis, a computer modeling was carried out for the initial stage of the reaction. The absorption at the lab. time of 10 μs, A_{10}, defined as $A_{10}=\ln(I_0/I_{10})$ where I_0 and I_{10} are the incident-light intensity and the transmitted intensity at the time respectively, is calculated and plotted in Fig. 3.

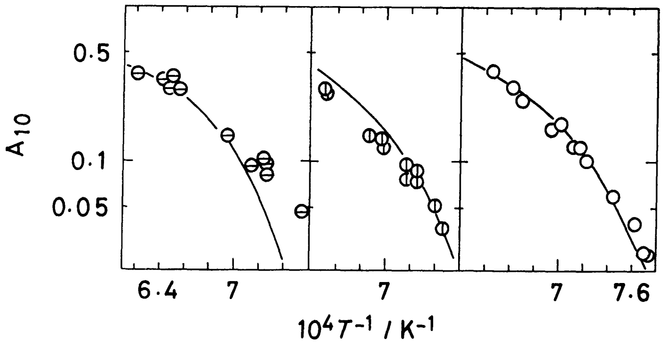

Fig. 3. The relation between A_{10} and $10^4/T$.
The symbols used are the same as those in Fig. 2.
The lines show modeled A_{10} for the three mixtures.

Table 1 shows the final reaction mechanism of the $n\text{-}C_4H_{10}$ pyrolysis assumed in this study. The reaction mechanism consists of 44 reactions with the maximum value of the rate larger than 10^{-7} (mol cm^{-3} s^{-1}) during the initial reaction period (10 μs). The rate constant of each reaction was taken from several sources except in a few cases. The k_{-1} value, the rate constant of the reverse reaction (−1), was estimated from the geometric mean rule using the following equation:

$$k_{-1} = k_{18}^2/(4k_{-31}[M]).$$

The k_{-31} value was evaluated from $k_{-31}=k_{31}/K_{31}$, where K_{31} is the equilibrium constant and [M]=density. The k values of the metathetical reactions, (3)—(8), were taken from those in the proposed reaction mechanism.[2,3] Each butyl radical has two channels for the decomposition. One of them is to H and butene, Reactions 9 and 10. The others are Reactions 11 and 12, which obey the β-bond breaking rule;[16] $n\text{-}C_4H_9$ decomposes to C_2H_4 and C_2H_5 and $s\text{-}C_4H_9$ to CH_3 and C_3H_6. Reactions 13—17 are primary steps in the butene pyrolysis. The k values adopted for Reactions 9—14 and 17 are those reported for the high pressure limit. Since these radical decompositions are expected to have different sensitivity spectra for the modeled A_{10} value, while their k values could be corrected for the fall-off with a similar factor, we left the k values of radical decompositions at the values shown in Table 1. In the reactions of the C_3 species, 18—30, their k values are taken mainly from

Table 1. Reaction mechanism and rate constants
$k=A\exp(-E/RT)$ (cm, mol, s, and kcal units)

	Reaction	log A	E	Ref.
1)	n-$C_4H_{10}=C_2H_5+C_2H_5$	$k_{-1}=10^{12.1}$		See text
2)	n-$C_4H_{10}=CH_3+n$-C_3H_7	13.9	71.9	This work
3)	C_2H_5+n-$C_4H_{10}=C_2H_6+n$-C_4H_9	14.0	22.8	3)
4)	C_2H_5+n-$C_4H_{10}=C_2H_6+s$-C_4H_9	13.5	20.1	3)
5)	CH_3+n-$C_4H_{10}=CH_4+n$-C_4H_9	14.7	20.9	3)
6)	CH_3+n-$C_4H_{10}=CH_4+s$-C_4H_9	14.7	18.2	3)
7)	$H+n$-$C_4H_{10}=H_2+n$-C_4H_9	15.1	16.7	3)
8)	$H+n$-$C_4H_{10}=H_2+s$-C_4H_9	15.0	14.0	3)
9)	n-$C_4H_9=C_4H_8(1)^*+H$	14.4	38.0	a)
10)	s-$C_4H_9=C_4H_8(2)^*+H$	14.4	37.5	a)
11)	s-$C_4H_9=CH_3+C_3H_6$	14.2	33.9	a)
12)	n-$C_4H_9=C_2H_4+C_2H_5$	13.6	29.0	a)
13)	$C_4H_8(1)=CH_3+C_3H_5$	16.9	73.0	b)
14)	$C_4H_8(2)=CH_3+C_3H_5$	16.0	80.0	c)
15)	$H+C_4H_8(1)=H_2+C_4H_7$	13.7	39.0	9)
16)	$H+C_4H_8(2)=H_2+C_4H_7$	13.7	38.0	9)
17)	$C_4H_7=C_2H_4+C_2H_3$	14.0	37.0	9)
18)	$CH_3+C_2H_5=C_3H_8$	12.9	0.0	17)
19)	$CH_3+C_3H_8=CH_4+i$-C_3H_7	12.6	10.3	d)
20)	$CH_3+C_3H_8=CH_4+n$-C_3H_7	12.6	10.3	d)
21)	$H+C_3H_8=H_2+i$-C_3H_7	13.8	8.0	e)
22)	$H+C_3H_8=H_2+n$-C_3H_7	13.8	8.0	e)
23)	i-$C_3H_7=C_2H_4+CH_3$	12.0	34.5	a)
24)	n-$C_3H_7=C_2H_4+CH_3$	13.8	33.2	a)
25)	i-$C_3H_7=H+C_3H_6$	14.3	41.3	a)
26)	n-$C_3H_7=H+C_3H_6$	13.8	38.0	a)
27)	$C_3H_6+M=C_2H_3+CH_3+M^{**}$	18.0	74.0	24)
28)	$C_3H_6=H+C_3H_5$	13.0	78.0	f)
29)	$H+C_3H_6=H_2+C_3H_5$	10.1	1.5	g)
30)	$C_3H_5=H+C_3H_4$	13.6	70.0	g)
31)	$C_2H_6+M=CH_3+CH_3+M$	111.3—25.26 log T	160.0	18)
32)	$C_2H_6+H=C_2H_5+H_2$	14.1	9.4	h)
33)	$C_2H_5+M=C_2H_4+H+M$	15.3	30.1	18)
34)	$CH_3+CH_3=C_2H_5+H$	14.9	26.6	10, 19)
35)	$CH_3+CH_3=C_2H_4+H_2$	16.0	32.0	10, 19)
36)	$C_2H_5+H=C_2H_4+H_2$	12.3	0.0	h)
37)	$CH_4+M=CH_3+H+M$	17.5	90.6	i)
38)	$CH_4+H=CH_3+H_2$	14.9	15.1	j)
39)	$C_2H_4+H=C_2H_3+H_2$	15.7	22.9	k)
40)	$C_2H_3+M=C_2H_2+H+M$	15.3	30.1	l)
41)	$CH_3+C_2H_5=CH_4+C_2H_4$	11.7	0.0	See text
42)	$C_2H_5+C_2H_5=C_2H_4+C_2H_6$	11.7	0.0	See text
43)	$CH_3+C_2H_4=CH_4+C_2H_3$	11.0	0.0	Assumed
44)	n-$C_4H_9=s$-C_4H_9	17.7	41.0	21)

a) S. W. Benson and H. E. O'Neal, "Nat. Stand. Ref. Data Ser.," NBS, No. 21 (1970). b) T. Kunugi, T. Sakai, K. Soma, and Y. Sakai, *Ind. Eng. Chem. Fundam.*, **9**, 314 (1970). c) P. Jeffers and S. H. Bauer, *Int. J. Chem. Kinet.*, **6**, 763 (1974). d) A. Lifshitz and M. Franklach, *J. Phys. Chem.*, **79**, 686 (1975). e) A. F. Trotman-Dickenson and G. S. Milne, "Nat. Stand. Ref. Data Ser.," NBS, No. 9 (1967). f) K. J. Laidler and B. W. Wojciechowski, *Proc. R. Soc. London, Ser. A*, **259**, 257 (1960). g) A. Amano and M. Uchiyama, *J. Phys. Chem.*, **67**, 1242 (1963). h) P. Camilleri, R. M. Marshall, and J. H. Purnell, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1434 (1974). i) W. C. Gardiner, Jr., T. Koike, and T. Tanzawa, in preparation. j) Th. Just and P. Roth, *Ber. Bunsenges. Phys. Chem.*, **79**, 682 (1975). k) Th. Just, P. Roth, and R. Damm, "16th Int. Symp. Combust.," The Combustion Institute, Pittsburgh (1977), p. 961. l) S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **71**, 1735 (1967). * $C_4H_8(1)$=1-butene and $C_4H_8(2)$=2-butene. ** $[M]=(4.0\pm0.3)\times10^{-6}$ (mol cm^{-3}).

those determined in the C_3H_8 pyrolysis study in shock waves.17) The k values of Reactions 31—40 are also taken form those derived in the C_2H_6 pyrolysis study in shock waves.18) In Reactions 31—40, the k values of the two channels of CH_3+CH_3 into C_2H_5+H and $C_2H_4+H_2$ were determined recently.10,19) Thus, the reaction mechanism in Table 1 has three channels for CH_3+CH_3, Reactions, −31, 34, and 35. The disproportionations, (41)—(43), which have only a minor effect on the modeling results, were included and their k values were assumed to be around 10^{11}; the ratios, k_{-1}/k_{42} and k_{18}/k_{41}, are expected to be larger than 1.[20] In comparison with the reaction mechanisms of the C_2H_6 and C_3H_8 previously reported,[17,18] it is characteristic of the 44-reaction mechanism that the isomerization reaction of C_4H_9, Reaction 44, is included.[21]

Our original computer program was devised to calculate the concentration of each species. To compare directly the computer modeling results with the A_{10} values shown in Fig. 3, the concentration of each species was converted to the absorption, A, in the program according to this equation:

$$A = \sum A_i = \sum C_i a_i d,$$

where A_i, C_i, and a_i are the absorption, the concentration, and the absorptivity of a species subscribed i respectively, and where d=optical path length (=7.2 cm). At 216 nm, the species which have large absorptivities are CH_3, C_3H_6, C_2H_4, and C_2H_2. The absorptivity of CH_3 was taken from the values previously reported[10,11] and was expressed by a 4th-order polynominal fit for the temperature. The absorptivity of the other three species were measured from the absorption at the shock front for mixtures diluted in Ar.[12,22] The following expressions of the absorptivity-temperature relation, together with that for CH_3, were incorporated in the computer program:

$$\log a(C_2H_4) = -3430/T + 6.66,^{12)}$$
$$\log a(C_2H_2) = -1829/T + 5.88,^{12)}$$
$$\log a(C_3H_6) = -3662/T + 8.15.^{22)}$$

The lines in Fig. 3 show the A_{10} values for the three mixtures modeled using the reaction mechanism shown in Table 1. We noticed the following disagreements in the two mixtures, though the lines almost went through the data points. In the 1% mixture, the modeled A_{10} value is smaller than the measured value at temperatures lower than 1400 K. The effect of the secondary reactions on the A_{10} value may be negligibly small under the present experimental conditions. Therefore, it is probable that the k_1 and/or k_2 values used are not appropriate to the modeling of the A_{10} value at these low temperatures. The k_2 values shown in Fig. 2 seem to be on a straight line at temperatures as low as 1290 K. However, the light attenuations due to the absorption measured at these low temperatures are small, and the k_2 value evaluated may have much larger data-reading errors than those at high temperatures. As for the k_1 value used, it can be adjusted so as to reproduce the experimental A_{10} value. No further fitting of the modeled A_{10} value to the measured value by adjusting these k values was done because Reactions (1) and (2) have a similar sensitivity for the A_{10}. In the 2% mixture, the modeled A_{10} is slightly larger than the measured one at high temperatures. However, we do not have any clear-cut explanations for the disagreement because almost the same sensitivity spectra were obtained for the 2 and 2.8% mixtures; a nice agreement between the two values is shown in Fig. 3 for the 2.8% mixture.

In the 2.8% mixture, the contributions to the modeled absorption are CH_3; 90%, C_3H_6; 6%, and C_2H_4; 3% at 1300 K and CH_3; 60%, C_3H_6; 27%, and C_2H_4; 12% at 1550 K, and it is found that the effect of C_2H_2 on the A_{10} value is negligible under the present experimental conditions. Thus, it is clear that, with an increase in the temperature, the products by the pyrolysis have much influence on the A_{10} value.

No further modeling for the reported experimental results[5-7] and for the absorption after 10 μs measured in this study were done. Propylene is one of the primary products in the n-C_4H_{10} pyrolysis, but the reaction mechanism of the C_3H_6 pyrolysis at high temperature has not yet been determined.[23] The reaction mechanism proposed by Burcat[24] is not satisfactory in explaining the experimental results measured by means of a 3.39-μm He-Ne laser absorption; that experiment was carried out under conditions similar to the present ones.[23] Since C_3H_6 is subjected to further decomposition as the reaction proceeds at these high temperatures, the ambiguity of the reaction mechanism may give an erroneous result for the modeled product distribution. Moreover, preliminary experimental results[22] by means of the absorption at 216 nm indicate that a large absorption by an unidentified product was measured in the C_3H_6 pyrolysis.

References

1) D. D. Hughes, R. M. Marshall, and J. H. Purnell, *J. Chem. Soc., Faraday Trans. 1*, **70**, 594 (1974).

2) P. D. Pacey and J. H. Purnell, *Int. J. Chem. Kinet.*, **4**, 657 (1972).

3) D. R. Powers and W. H. Corcoran, *Ind. Eng. Chem., Fundam.*, **13**, 351 (1974).

4) G. L. Pratt and D. Rogers, *J. Chem. Soc., Faraday Trans. 1*, **75**, 2688 (1979).

5) T. P. Izod, G. B. Kistiakowsky, and S. Matsuda, *J. Chem. Phys.*, **56**, 1377 (1972).

6) Y. Yoshida, W. Hirose, M. Kitazaki, and F. Kagano, *Proc. 11th Shock Tube Symp.*, Univ. of Washington Press, Seattle (1977), p. 358.

7) K. Fritz and H. Grönig, *Proc. 11th Shock Tube Symp.*, Univ. of Washington Press, Seattle (1977), p. 383.

8) D. L. Allara and D. Edelson, *Int. J. Chem. Kinet.*, **7**, 479 (1975).

9) K. M. Sundaram and G. F. Froment, *Ind. Eng. Chem., Fundam.*, **17**, 174 (1978).

10) T. Tsuboi, *Jpn. J. Appl. Phys.*, **17**, 709 (1978).

11) K. Glänzer, M. Quack, and J. Troe, *16th Int. Symp. Combust.*, The Combustion Institute, Pittsburgh (1977), p. 949.

12) T. Koike and K. Morinaga, *Bull. Chem. Soc. Jpn.*, in press.

13) W. C. Gardiner, Jr., B. F. Walker, and C. B. Wakefield, "Shock Waves in Chemistry," ed by A. Lifshitz, Dekker, New York (1980), Chap. 1.

14) G. Hertzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand, N. Y. (1966), Vol. 3.

15) D. A. Parkers and C. P. Quinn, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1952 (1976).

16) D. A. Leathard and J. H. Purnell, *Ann. Rev. Phys. Chem.*, **21**, 197 (1970).

17) T. Koike and W. C. Gardiner, Jr., *J. Phys. Chem.*, **84**, 2005 (1980).

18) D. B. Olson, T. Tanzawa, and W. C. Gardiner, Jr.,

Int. J. Chem. Kinet., **11**, 23 (1979).

19) K. A. Bhaskaran, P. Frank, and Th. Just, *Proc. 12th Shock Tube Symp.*, Hebrew Univ. Press, Jerusalem (1980), in press.

20) S. W. Benson, *Adv. Photochem.*, **2**, 1 (1964).

21) M. C. Lin and M. H. Back, *Can. J. Chem.*, **44**, 2369 (1966).

22) T. Koike and K. Morinaga, unpublished results.

23) T. Koike and W. C. Gardiner, Jr., in preparation.

24) A. Burcat, *Fuel.*, **54**, 87 (1975).