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Relative Reactivities of C–H Bonds in H Atom Abstraction by Phenyl Radicals

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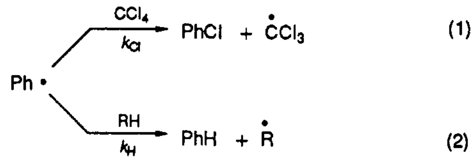
Relative reactivities of different primary, secondary, and tertiary C–H bonds in saturated hydrocarbons in the reaction with the phenyl radical have been determined by using T-labeled compounds. At low temperatures and in the liquid phase the selectivity of the phenyl radical is similar to that of the methyl radical, whereas at about 900 K in the gas phase the phenyl radical reacts less selectively. Average relative reactivities of primary, secondary, and tertiary C–H bonds are 1:8.5:50 at 373 K and 1:2:3 at about 900 K. C–H bonds in highly branched hydrocarbons like isooctane have different reactivities.

Phenyl radicals react with saturated hydrocarbons by H abstraction exclusively. The present knowledge on relative reactivities of different kinds of C–H bonds toward phenyl radical attack is due to the comprehensive paper of Bridger and Russell[1] in 1963, who measured the H-donor ability of 104 compounds at 333 K. They used the Cl abstraction from carbon tetrachloride as a standard reaction, and they measured the competition between H and Cl abstraction as the ratio of the products benzene and chlorobenzene (Scheme I). This method gives the relative reactivities of individual types of C–H bonds only indirectly. In some cases it fails, e.g for isooctane. The experimental technique described in ref 1 is restricted to the liquid phase and consequently to relatively low temperatures. Since Bridger and Russel the reactions of phenyl radicals in solution have been the subject of some studies,[2-5] but a reliable absolute basis for rate constants of reactions of unsubstituted phenyl radicals has been given only by Lorand et al.[6] and Scaiano and Steward.[7] The rate constant for the most frequently used standard reaction—the Cl abstraction from CCl_4—was measured as $k_{Cl} = (3.7 - 5.8) \times 10^6\ M^{-1}\ s^{-1}$ at 318 K in benzene–carbon tetrachloride mixtures[6] and as $k_{Cl} = (7.8 \pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$ at 298 K in Freon 113.[7] Taking k_{Cl} from the only direct, time-resolved measurement of Scaiano and Steward,[7] who used the laser flash photolysis technique, and an estimated activation energy of about 5 kcal/mol,[8] it follows that $k_{Cl} = 3.6 \times 10^{10} \exp(-5.000/RT)\ M^{-1}\ s^{-1}$.

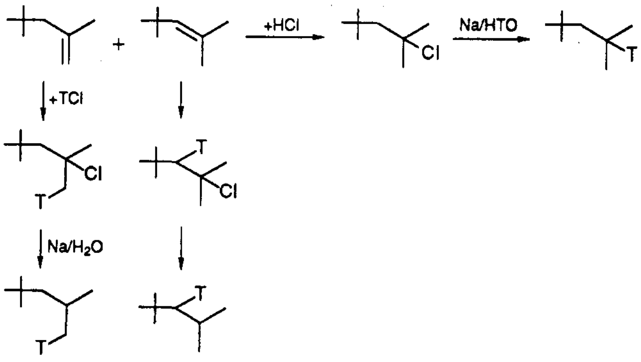
In contrast to liquid-phase reactions no kinetic data on gas-phase reactions of phenyl radicals have been published as far as we know.

In this study we used tritium (T)[9] labeled hydrocarbons as competitive partners in H abstractions by phenyl radicals to get quantitative information on site specificity of the radical attack in the liquid phase as well as in the gas phase at temperatures typical of hydrocarbon pyrolysis. The method, based on competition between C–H and C–T bonds, was widely used in the 60s by Berezin et al.[10] and by Szwarc et al.[11] for studying H abstraction by methyl radicals, but later on it went out of fashion.[12,13]

Scheme I



Scheme II



Methods

Phenyl Radical Precursors. Dibenzoyl peroxide (DBPO) and *trans*-azobenzene were used as phenyl radical precursors. DBPO was recrystallized from a chloroform–methanol mixture and dried in vacuum over molecular sieves. *trans*-Azobenzene from Merck (mp = 67–68 °C, GLC 98%) was taken without further purification.

Labeled Hydrocarbons. The T-labeled hydrocarbons listed in Table I were synthesized by hydrolysis of the

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[1] Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754.

[2] (a) Pryor, W. A.; Guard, H. *J. Am. Chem. Soc.* **1964**, *86*, 1150. (b) Pryor, W. A.; Echols, J. T., Jr.; Smith, K. *Ibid.* **1966**, *88*, 1189. (c) Pryor, W. A.; Fiske, Th. R. *Trans. Faraday Soc.* **1969**, *65*, 1865.

[3] Levin, Ya.; Abulchanov, A. G.; Nefedov, V. P.; Skorobatova, M. S.; Iwanov, B. E. *Dokl. Akad. Nauk SSSR* **1977**, *235*(3), 629.

[4] Madhavan, V.; Schuler, R. H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 888.

[5] Migita, T.; Takayama, K.; Abe, Y.; Kosugi, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1137.

[6] (a) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589. (b) Lorand, J. P.; Kryger, R. G.; Herron, N. R. *Colloq. Int. CNRS (1977) Radicause Libres Org.* **1978**, 463.

[7] Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

[8] (a) Griller, D. *Ann. Rep. Prog. Chem. Sect. B* **1985**, 86–89. (b) Jewell, D. R.; Mathew, L.; Warkentin, J. *Can. J. Chem.* **1987**, *65*, 311. (c) The value $E_A = 8.2 \pm 1.5$ kcal/mol of Kasukhin et al. (Kasukhin, L. F.; Ponomarchuk, M. P.; Buchachenko, A. L. *Chem. Phys.* **1974**, *3*, 136) measured by CIDNP in CCl_4 in the temperature range 316–336 K seems us to be too high.

[9] In this paper the capital T is used as symbol for the ^3H isotope tritium.

[10] (a) Antonovski, V. L.; Berezin, I. V. *Dokl. Akad. Nauk SSSR*, **1959**, *127*(1), 124. (b) Antonovski, V. L.; Berezin, I. V. *Ibid.* **1960**, *134*(4), 860. (c) Berezin, I. V.; Wazek, K.; Go-Tschu; Dobish, O.; Kasanskaya, N. F. *Trudy po Khim. Khim. Technol.* **1961**, *4*(1), 18; *Chem. Abstr.* **1962**, *56*, 3324. Dobish, O. Thesis, Moskow University, 1962. (d) Berezin, I. V.; Kasanskaya, N. F. *J. fiz. Khim.* **1962**, *36*, 1800. (e) Berezin, I. V.; Dobish, O. *Dokl. Akad. Nauk SSSR* **1962**, *144*(2), 374. (f) Berezin, I. V.; Kasanskaya, N. F.; Pentin, Ju. A. *J. fiz. Khim.* **1964**, *38*(1), 125.

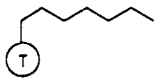
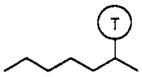
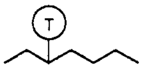
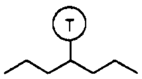
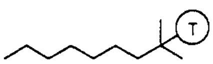
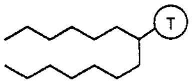
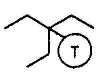
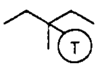
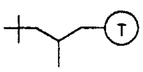
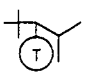
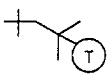
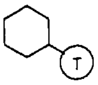
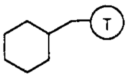
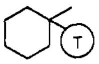
[11] Eachus, A. E.; Meyer, J. A.; Pearson, J.; Swarc, M. *J. Am. Chem. Soc.* **1968**, *90*, 3646.

[12] Hendry, G. D.; Mill, T.; Piszkiewicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937.

[13] Landolt-Börnstein. New Series. *Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Parts a–e.

0022-3263/89/1954-3571$01.50/0

Table I. Relative Molar Radioactivities of Benzene Formed from Phenyl Radicals ($Ph^{\bullet} + R\text{-}T \rightarrow Ph\text{-}T + R^{\bullet}$) at 100 °C in *n*-Heptane

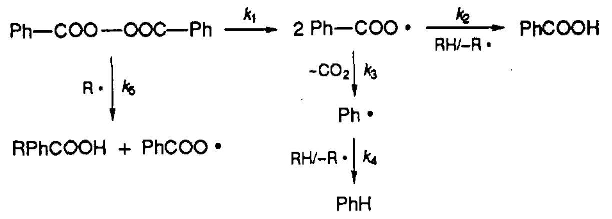
labeled hydrocarbon R–T	$10^3 a_{benzene}$		$\pm S$,[a] %	n[b]	r_{C-T}[c]	r_{C-H}[d]
	1.12		1	4	1.00	1.00
	9.65		5	2	8.6	9.3
	10.0	10.6[e] 9.6[f]	5	5	8.9	9.3
	8.8		2	2	7.9	9.3
	61.8		–	1	55.2	44
	9.0		2	2	8.0	9.3
	52.8	53.0[a] 52.2[f]	0.2	2	47.1	44
	59.9		–	1	53.5	44
	1.70		1	4	1.52	-
	4.65		10	4	4.2	-
	11.9		5	4	10.6	-
	12.3		7	2	11.0	9.2
	1.10		2	3	0.98	1.00
	70.2		3	2	62.7	63

[a] One standard deviation of the single values. [b] Number of experiments. [c] Relative reactivity of the C–T bond, this paper. [d] Relative reactivity of the C–H bond at 60 °C, Bridger and Russell.[1] [e] Starting concentration of DBPO is 0.2 M and 0.1 M ([f]) instead of 0.4 M as for the other experiments.

corresponding alkylmagnesium halides with HTO. Their specific activity was in the range of 3–50 MBq g^{-1}. As the criterion for the purity of labeling in the desired position exclusively we took the capillary GLC of the preceding haloalkanes which indicated isomer purities >99%. The routes to haloalkanes are well established: conversion of primary, secondary, and tertiary alcohols with HBr, $SOCl_2$/pyridine, and HCl, respectively. For the labeling of isooctane (2,2,4-trimethylpentane), we started from the pure trimethyl-1- and -2-pentene (isolated from a diisobutene fraction by preparative GLC), which were converted by HCl or TCl addition to the tertiary chloride according to Scheme II. The reduction of this tertiary isooctyl chloride by reaction with magnesium, however, yielded isooctane besides isooctenes predominantly by disproportionation. Therefore we reduced it with Na in ether plus H_2O or HTO with good yields. To check the labeling position inside the resulting isooctanes we made all synthesis steps with D_2O instead of HTO and detected it by ^2H NMR spectroscopy because the specific activity of the labeled hydrocarbons is too low for ^3H NMR analysis; 99% of the deuterium was found in the desired positions. All labeled hydrocarbons were finally purified by preparative GLC.

Apparatus and Procedure. We carried out our liquid-phase experiments with a 0.4 M solution of DBPO in *n*-heptane (2 mL) to which up to 5 mol % of the T-labeled hydrocarbon was added. This mixture was heated under reflux for 2.5 h in an open glass vessel, and the CO_2 formation was measured volumetrically. After addition of 2 mL of *n*-dodecane the reaction product was extracted with NaOH (1 M, 3 mL) and distilled. The distillate containing chiefly *n*-heptane, the formed benzene (≈5%), heptenes (<1%), and the labeled products (if $\leq C_8$) was divided by preparative GLC into pure *n*-heptane, benzene, and the unconverted labeled hydrocarbon, which was available for further use. To guarantee the purity of the isolated benzene, the separation was made on two columns with phases of different polarities. The background for the relative molar activity of the benzene ($a_{benzene}$) isolated in such a way was estimated to be $\leq 2 \times 10^{-5}$. All measurements of activity were made by liquid scintillation counting. The gas-phase experiments were conducted in a flow system with use of an electrically heated reactor tube of

Scheme III



quartz glass (4 × 0.7 × 200 mm, $V_R \approx 0.3$ cm^3) surrounded by a stainless steel tube and on-line coupled to a radio gas chromatograph. The apparatus worked in a pulse regime; 5 μL of a solution of about 5 mol % of azobenzene in a labeled hydrocarbon was injected into a hot carrier gas stream (2 1h^{-1} He at 0.17 MPa), which passed the reactor tube with a residence time of about 0.1 s at temperatures between 600 and 700 °C. The pyrolysis products inclusive of benzene were analyzed on a 6 m × 4 mm Carbowax column at 65 °C. The radio GLC had to ensure the correct determination of the ratio of the specific activities of the formed benzene and the labeled unconverted hydrocarbon despite the low activity content (0.1–0.2%) of the benzene. We used a TCD as a mass detector and a flow proportional counter tube (10 ccm) as a radioactivity detector.

Results

Decomposition of DBPO. The thermal decomposition of DBPO in the liquid phase is well established[14-21] (Scheme III). Besides the spontaneous decomposition (k_1) there is also an induced decomposition path (k_5) giving substituted benzoic acid. At 100 °C, we found a pure first-order rate constant for the CO$_2$ formation equal to 5×10^{-4} s^{-1} in 0.4 M n-heptane solution. From 1 mol of DBPO 1.25 ± 0.1 mol of CO$_2$ and benzene (ratio 1:1 ± 0.05) plus 0.75 ± 0.1 mol of benzoic acids were formed. The acidic fraction extracted contained about 70% unsubstituted benzoic acid and 30% heptylbenzoic acid, which was identified by ^{1}H NMR spectroscopy as a mixture of the ortho and para isomers. The kinetic data and the product distribution reported are in full accordance with the literature.[22] The run time of 2.5 h corresponds to 6.5 half-life periods and 97% DBPO conversion.

The activity content of the acidic fraction is composed of a very high contribution from the alkyl groups in the substituted benzoic acids and of a very low one from the carboxylic hydrogen. This portion is a measure for the selectivity of H abstraction by the benzoyloxy radical. It can be easily separated from the whole activity by H–T exchange, which occurs quickly during extraction with aqueous NaOH. We measured the activity of the purified water and calculated the relative molar activities of the carboxyl hydrogen ($a_{\text{-COOH}}$). These values are in the same range as those for benzene (Table I), but they are less reproducible. Typical $a_{\text{-COOH}}$ values are $(3 \pm 1) \times 10^{-3}$ for primary C–H bonds, $(10–20) \times 10^{-3}$ for secondary and $(30–50) \times 10^{-3}$ for tertiary ones. Besides these values which could be regarded as roughly in line with our expectations, we found some surprisingly high $a_{\text{-COOH}}$ values for primary C–H bonds placed in vicinity to tertiary C atoms ($(19 \pm 1) \times 10^{-3}$ for [*methyl*-T]methylcyclohexane, $(22 \pm 1) \times 10^{-3}$ for [5-T]-2,2,4-trimethylpentane). Therefore we feel that our treatment of the data does not give a real picture of the selectivity of the benzoyloxy radical in H abstraction reactions. Possibly there are yet other sources of bringing activity into the carboxyl group (e.g., induced decomposition whose intermediates are not fully elucidated or active participation of the benzoyloxy radical in disproportionation reactions) which make it unsuitable as key value at least under the conditions of the rather high DBPO concentrations used in these experiments.

Formation of Benzene from DBPO. The phenyl radicals generated in the DBPO decomposition react completely to benzene by H abstraction (k_4) under the reaction conditions used. The relative molar activity of benzene is defined as

$$a_{\text{benzene}} = \frac{\text{molar activity of benzene}}{\text{molar activity of hydrocarbon mixture}}$$

To guarantee that a_{benzene} reflects the competition between H and T abstraction from the starting hydrocarbons exclusively (and not from intermediates or from reaction products), we varied the starting concentration of DBPO. The data given in Table I prove that a 4-fold variation of DBPO concentration does not influence a_{benzene} significantly.

Bridger and Russell[1] used phenylazotriphenylmethane (PAT) as phenyl radical precursor because the triphenylmethyl radical formed acts as a very efficient trapping agent, and therefore it prevents radical chain reactions. We measured the activity of purified n-heptane after DBPO decomposition in the presence of T-labeled hydrocarbons other than n-heptane to check our system for chain reactions. a_{heptane} values $\leq 0.5 \times 10^{-3}$ for experiments with hydrocarbons labeled in secondary and tertiary positions indicate that no significant redistribution of tritium between the saturated hydrocarbons occurs. The very small activity content in n-heptane can be explained by radical disproportionation reactions; radical chain reactions are negligible. This assertion holds only for pure hydrocarbon mixtures, whereas radical chain reactions occur in the presence of carbon tetrachloride (see below).

Relative Rate Constants k_H:k_{Cl}. To put the relative reactivities of C–H bonds determined in this paper on the basis of absolute rate constants it is useful to measure relative rate constants in competition experiments with the participation of a component for which absolute rate constants of phenyl radical attack are available. For this reason we decomposed DBPO (0.4 M) in n-heptane–carbon tetrachloride mixtures (molar rations 0.33 and 0.66) and calculated k_H:k_{Cl} directly from the product ratio of benzene to chlorobenzene extrapolated to zero conversion. This extrapolation is necessary because of the high reactivity of chloroform as H donor. Chloroform and chloroheptanes are formed as the main products of a radical chain process. Its occurrence is a disadvantage of DBPO as phenyl radical source in comparison to PAT, but the decomposition of DBPO (0.4 M) in pure carbon tetrachloride at 80 °C gave

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(14) (a) Walling, Ch.; Savas, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 1738. (b) Walling, Ch.; Cekovic, Z. *Ibid.* **1967**, *89*, 6681. (c) Walling, Ch.; Azar, J. C. *J. Org. Chem.* **1968**, *33*, 3885.

(15) (a) De Tar, D. F.; Long, R. A. J.; Rendleman, J.; Bradley, J.; Duncan, P. *J. Am. Chem. Soc.* **1967**, *89*, 4051. (b) De Tar, D. F. *Ibid.* **1967**, *89*, 4058.

(16) (a) Swain, G.; Stockmayer, W. H.; Clark, J. T. *J. Am. Chem. Soc.* **1950**, *72*, 5426. (b) Swain, G.; Schaad, L. J.; Kreske, A. J. *Ibid.* **1958**, *80*, 5313.

(17) Schwerzel, R. E.; Lawler, R. G.; Evans, G. T. *Chem. Phys. Lett.* **1974**, *29*, 106.

(18) Janzen, E. G.; Evans, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 205.

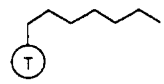
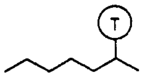
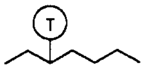
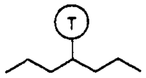
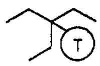
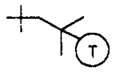
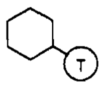
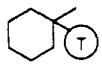
(19) Yamauchi, S.; Hirota, N.; Takahara, S.; Sakuragi, H.; Tokumaru, K. *J. Am. Chem. Soc.* **1985**, *107*, 5021.

(20) Kim, S. S.; Seo, J. S.; Yoon, M. H. *J. Org. Chem.* **1987**, *52*, 3691.

(21) (a) Grossi, L.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1985**, *50*, 5882. (b) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 897; **1988**, *110*, 2877 and 2886.

(22) From the latest data of Ingold et al.[21b] on the BPO radical reactions we estimate a ratio of rates of decomposition and H abstraction of about 5:1 under the conditions used here. We attribute the greater portion of benzoic acids found by us to the induced decomposition of DBPO.

Table II. Relative Molar Radioactivities of Benzene Formed from Phenyl Radicals ($Ph^{\bullet} + R\text{-}T \rightarrow Ph\text{-}T + R^{\bullet}$) at About 650 °C

labeled hydrocarbon R-T	T_R, °C	conversion of R-T, %	$10^2 a_{benzene}$	$\pm S$,[a] %	n[b]	r_{C-T}[c]
	630–730	14–43	1.8	10	12	1.0
	650–700	20–35	3.6	8	7	2.0
	630	25	3.2	3	7	1.8
	610–635	25–40	3.6	8	11	2.0
	610–665	11–23	4.6	5	14	2.7
	640–670	7–12	5.2	4	5	3.3
	615–625	5–11	3.4	4	7	2.0
	605–615	5–7	5.5	10	6	2.8

[a–c] The same as in Table I.

a ratio of benzene to chlorobenzene ≤0.01, whereas PAT yields a ratio of 0.13 at 60 °C and a starting concentration of 0.2 M by cage processes and side reactions.[1] From this point of view DBPO is superior as phenyl radical source, because the blank value of benzene formed from PAT had to be corrected. Besides chlorobenzene-substituted benzoic acids (about 0.9 mol per mole of DBPO decomposed) are also formed in carbon tetrachloride, indicating that the induced decomposition dominates over the spontaneous one. Control experiments with added benzoic acid confirmed the view that the reactivity of the carboxyl group as hydrogen donor is negligible. The ratio k_H:k_{Cl} = 0.965 ± 0.015 obtained at about 90 °C is identical with the value of 0.965 ± 0.015 at 60 °C given by Bridger and Russell.[1] Taking into account all the C–H bonds in n-heptane, the absolute rate constant of phenyl radical attack on a particular C–H$_i$ bond in any hydrocarbon at 100 °C is given by $k_{C-H} = k_{Cl} r_i n_i / (\sum_j n_j r_j)_{n\text{-heptane}}$ with $k_{Cl} = 1.2 \times 10^8$ M^{-1} s^{-1}, r_i = relative reactivity of the C–H$_i$ bond under consideration, n_i = number of equivalent C–H$_i$ bonds in the molecule, and $(\sum_j n_j r_j)_{n\text{-heptane}} = 91.8$.

Formation of Benzene from Azobenzene. An important difference between the product distribution in experiments at 100 °C and at 600–700 °C consists in the possible formation of benzene from the labeled saturated hydrocarbons themselves at high temperatures. The low activity content of the benzene formed from phenyl radicals requires a careful check of the blank value of benzene formation. All the $a_{benzene}$ values given in Table II are corrected considering this. The hydrocarbon conversion was kept low enough so that the portion of the activity blank value in benzene was smaller than 20% of the total.

It was the aim of our investigation to come as near as possible to the temperature range typical of the spontaneous decomposition of paraffins and naphthenes. Appropriate phenyl radical precursors appear to be azobenzene and benzil. Both compounds give high benzene yields[23-25] besides exclusively inert products and prevent the generation of radicals other than phenyl.

To study H transfer reactions it is inevitable to exclude halogen compounds carefully. Especially, hydrogen bromide acts as a very efficient H-transfer catalyst.[26-29] For this reason all radical sources containing halogens were avoided. Benzil was found to be slightly too stable, so we chose azobenzene. Kinetic data on its decomposition (E_A = 53.4,[30] 66.3[25] kcal/mol) available up to 440 °C give a rate constant of 7.4 s^{-1} at 650 °C independent of hydrocarbon admixtures.[25] The resulting half-life period of 0.1 s corresponds to the residence time realized in our flow experiments. Though there are not any detailed mechanistic studies on azobenzene pyrolysis at temperatures >450 °C, we see no reason against the concept of a pure reaction according to $Ph\text{-}N = N\text{-}Ph \rightarrow 2Ph^{\bullet} + N_{2\bullet}$. We found benzene yields of 10–90% from azobenzene as component of hydrocarbon mixtures in the temperature range 600–700 °C. The relative molar activities of benzene given in Table II do not show a significant temperature dependence within the range investigated. By control experiments it was established that benzene is not subject to a H-exchange reaction under the pyrolysis conditions used. Unlike the liquid-phase experiments we used pure T-labeled hydrocarbons undiluted with n-heptane as H donors in the gas-phase experiments. This procedure was necessary because of the lower activity detection limit of radio

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(29) We found that only traces of bromine compounds in, e.g., isooctane changed the pyrolysis product composition in such a way that isobutane was increased by 2 orders of magnitude presumably as result of the reaction *tert*-butyl + HBr → isobutane + Br.

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GLC in comparison with liquid scintillation counting. This is also the reason for the reduction in the number of labeled hydrocarbons included in Table II. The remaining ones had specific activities too low for a reliable measurement of benzene activity. The relative reactivities given in Table II were calculated from a_{benzene}, taking into account the different overall reactivities ($\sum_j n_j r_j$) of the labeled hydrocarbons as follows:

$$r_i = \frac{a_{\text{benzene}}(\text{from R-T}_i)}{a_{\text{benzene}}(\text{from [1-T]}n\text{-heptane})} \times \frac{(\sum\limits_j n_j r_j)_{\text{R-T}_i}}{(\sum\limits_j n_j r_j)_{n\text{-heptane}}}$$

For example, all the primary and secondary C–H bonds in 3-ethylpentane were assumed to have the same reactivities r_j as those in n-heptane.

By analogy with the liquid-phase experiments we performed also a series of pyrolysis runs with an excess of n-heptane as H donor at 600 °C. The relative molar activities of benzene isolated by preparative GLC, however, are more doubtful for experimental reasons. The measured values of a_{benzene} (0.022, 0.051, 0.063 for [1-T]n-heptane, [2-T]n-heptane, [3-T]-3-ethylpentane) and the resulting relative reactivities ($r_{\text{primary}}:r_{\text{secondary}}:r_{\text{tertiary}} = 1:2.3:2.9$) are close to those given in Table II.

Discussion

Kinetic Isotope Effect (KIE). From the equation $k_H/k_T = r_i/(a_{\text{benzene}}\sum_i n_i r_i)$ we calculated the primary KIE for secondary C–T bonds in n-heptane at 100 °C in the liquid phase to be 9.7 and in cyclohexane at 620 °C in the gas phase to be 2.45. From both values it follows that $k_H/k_T = 0.9 \exp(1.750/RT)$. We do not know any comparable KIE's for phenyl radical attack on C–T bonds from the literature. Only for methyl radical attack are some k_H/k_T values available. Szwarc et al.[11] gave $k_H/k_T = (1.0 \pm 0.5) \exp(2.700/RT)$ in the temperature range 0–95 °C for benzylic C–H bonds. Similar KIE's were found by Berezin et al.,[10] e.g., $k_H/k_T = 0.18 \exp(3.440/RT)$ and $k_H/k_T = 17.8$ at 100 °C for n-heptane in the temperature range 60–100 °C.[10d] From results of 2-T-labeled isobutane pyrolysis we deduced $k_H/k_T = 4.8 \pm 0.3$[31] at 600 °C for methyl radical attack on the tertiary C–T bond. The lower KIE of phenyl radical attack in comparison to that of methyl radicals is obvious. This is in line with findings of Pryor and Fiske[2c] for hydrogen abstraction from the S–H group in n-heptyl mercaptan at 60 °C by methyl radicals ($k_H/k_T = 3.3$) and by phenyl radicals ($k_H/k_T = 2.0$). If we take the inverse KIE as a measure of reactivity of a radical[32] then our data support the view of a very high reactivity of phenyl radicals in H abstraction.

From the good conformity of the relative reactivities of primary, secondary, and tertiary C–H bonds determined by Bridger and Russell[1] with the corresponding values for C–T bonds determined in the present paper (Table I), we conclude that there are no significant differences in the KIE's for the phenyl radical attack on these bonds. This assertion is the premise for discussing measured reactivities of C–T bonds like those of C–H bonds in unlabeled hydrocarbons.

Relative Reactivities at 100 °C. All relative reactivities (r_i) are normalized to the reactivity of a primary C–T bond in n-heptane, which is measured precisely (Table I). The primary C–T bond in methylcyclohexane has the same reactivity, whereas that positioned in isooctane is more reactive by about 50%. This finding is rather suspicious but certain from the experimental point of view. It will be discussed later.

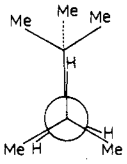

Figure 1.

All secondary C–T bonds in n-alkanes have practically equal reactivities. No significant influence of the chain length or of the position within the alkane is obvious. Similar results were given by Berezin et al.[10] for methyl radical attack on T-labeled n-heptanes, e.g., at 90 °C $r_1:r_2:r_3:r_4 = 1:9.23:9.29:9.17$. The secondary C–T bonds in cyclohexane were found to be more reactive by about 30% than secondary ones in n-alkanes. This result is in contrast to the data set of Bridger and Russell,[1] who found identical values. A possible explanation of the increased reactivity of cyclohexane could be the presence of axial C–H bonds, which differs slightly from ordinary secondary ones due to their Pitzer strain.

The tertiary C–T bonds in paraffins have an average reactivity $r_{\text{tert}} = 51 \pm 4$. There is a slight tendency for the reactivity to increase with increasing number of methyl substituents at the tertiary C atom, but it is not significant. Again the tertiary C–T bond in methylcyclohexane is more reactive than tertiary C–T bonds in isoalkanes by about 20%. In this case our r value is identical with that of Bridger and Russell.[1]

The isooctane molecule is to be considered as an exceptional case with respect to the reactivity of its C–H bonds by reason of extensive steric strains and hindrance. In this very case the labeling method is obviously superior to other techniques. Bridger and Russell[1] found only 35–36% reactivity for isooctane in comparison to n-heptane as H donor and deduced from this a negligibly low reactivity of the tertiary C–H bond. Actually, the tertiary as well as the secondary C–H bonds are much less reactive (Table I). The gross reactivity of isooctane is calculated to be 40% referred to n-heptane on the basis of our r values assuming "normal" reactivities for the methyl groups in the vicinity of the quarternary C atom. From Berezin's data[10f] follow a gross reactivity of 40% and a ratio of reactivities of tertiary and secondary C–T bonds in isooctane of 0.52 in methyl radical attack at 90 °C. But we feel some doubt about the isotopic purity of secondary T-labeled isooctane prepared by grignard reduction. Isooctane exists in the liquid phase in a preferred conformation of the molecules, in which the tertiary H atom is additionally blocked by two methyl groups of the neopentyl group (Figure 1).

This can be classified as a typical front-strain effect. It makes the approach of a radical more difficult. Some convincing results on the influence of the preference of conformations on the reactivity of C–H bonds in H abstraction were published by Szwarc et al.,[11] e.g., $r_{\text{tetralin}}:r_{\text{bibenzyl}} = 4.9$ at 95 °C in methyl radical attack. Besides the front-strain effect there are some considerable back-strain effects in the isooctane molecule increasing the reactivities of C–H bonds. This applies, e.g., to the methyl groups, the reactivity of which was found to be raised by about 50% in relation to ordinary methyl groups. A similar increase in reactivity (about 60%) was deduced for the axial C–H bonds in cyclohexane.

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If we compare the methyl and the phenyl radical with respect to their reactivity, then clearly the latter is much more reactive ($k_{\mathrm{Ph\bullet+sec\text{-}C\text{-}H}} \approx 10^7$ M^{-1} s^{-1},[7,13] $k_{\mathrm{Me\bullet+sec\text{-}C\text{-}H}} \approx 10^2$ M^{-1} s^{-1} at 373 K[12,13,33,34]). This is in line with the C–H bond strength in benzene and methane (BDE = 111 and 105 kcal/mol,[35] respectively). Contrary to this, both radicals attack C–H bonds with very similar selectivities, e.g., $r_{\mathrm{primary}}:r_{\mathrm{secondary}}:r_{\mathrm{tertiary}}$ = 1:8.5:50 for phenyl radicals at 100 °C (this paper) and 1:10:ca. 100[10e] at 80 °C or 1:4.3:46[36] at 110 °C for methyl radicals. This similarity holds also for different C–H bonds in allylic and benzylic positions.

We are not in a position to give a convincing interpretation of the relation between reactivity and selectivity in hydrogen abstraction reactions by the two carbon centered radicals. The absence of such a relation was already asserted by Lorand et al.[6]

Relative Reactivities at 650 °C. From the relative reactivities compiled in Tables I and II it follows that

$$\frac{k_{\mathrm{secondary}}}{k_{\mathrm{primary}}} = 0.75 \exp(1.800/RT)$$

$$\frac{k_{\mathrm{tertiary}}}{k_{\mathrm{primary}}} = 0.45 \exp(3.500/RT)$$

if a linear Arrhenius plot is assumed for a temperature range of 550 K. These ΔE_{A} values correspond precisely to the values given by McNesby et al.[37] for methyl radicals (300–470 °C, 1.75 and 3.5 kcal/mol, respectively). The ratios of the A factors calculated from our data appear more reasonable than those given by McNesby ($A_{\mathrm{secondary}}/A_{\mathrm{primary}} = 1.30$, $A_{\mathrm{tertiary}}/A_{\mathrm{primary}} = 1.43$), because the approach of the attacking radical to a C–H bond is clearly rendered more difficult in the direction from primary to tertiary ones.

In the high-temperature region the phenyl radical exhibits the expected low selectivity in H abstraction: $r_{\mathrm{primary}}:r_{\mathrm{secondary}}:r_{\mathrm{tertiary}} \approx$1:2:3 at about 650 °C.

Corresponding values for methyl radical attack are $r_{\mathrm{primary}}:r_{\mathrm{secondary}}:r_{\mathrm{tertiary}} \approx$ 1:3.3:10 at 700 °C.[31,38] A treatment of relative reactivities in methyl radical attack in the low- and the high-temperature region to calculate ΔE_{A} values by analogy with the phenyl radical reaction as made above does not yield reasonable results, presumably by reason of nonlinear curves in the Arrhenius coordinates.[39]

The "normal" reactivity of the tertiary C–H bond in isooctane is readily explained by the fact that the dominance of a particular conformation is canceled in the gas phase at 650 °C although the back-strain effect in the isooctane molecule is retained and seems to raise slightly the reactivity of the tertiary C–H bond.

The labeling method applied in the current study offers relative reactivities of C–T bonds in radical reactions over a large temperature range. It is open for extension to other types of substrates and, in combination with appropriate radical sources, to other abstracting radicals. Further investigations are in progress.

Experimental Section

The radioactivity of liquid samples was measured with a Packard TRI-CARB 3390 scintilation spectrometer in standard cocktails. For the preparative GLC separation and purification of substances we used a self-made equipment which permitted injections up to a 1-mL sample per run. The columns were 4 m × 2 cm 15% poly(ethylene glycol) on sterchamol and 6 m × 1 cm 15% SE 30 on sterchamol.

Labeled Compounds. Most T-labeled compounds were prepared by hydrolysis of the corresponding alkylmagnesium halides (chlorides or bromides) with HTO according to the following procedure: 50 mmol of alkyl halide were converted with an excess of magnesium (70 mmol) as chips or powder (for tertiary chlorides) in 50–100 mL of dry ether. After the end of the dropwise addition of the alkyl halide within 1 h, the mixture was kept on reflux for an additional hour and cooled down to 0 °C, and 1 mL of tritiated water (specific activity ca. 500 MBq g^{-1} was added under cooling and vigorous stirring. Ten minutes after that the precipitate formed was dissolved with 20 mL of half-concentrated hydrochloric acid. The ether phase was washed with Na_2CO_3 solution and water and dried over Na_2SO_4. After the ether was removed the hydrocarbon was distilled, bromine was added dropwise to a brownish colour, and it was washed with Na_2CO_3 solution, dried, and distilled again. These hydrocarbons obtained with yields of 50–80%, having a purity of 98–99% already, were finally purified by preparative GLC. Their specific activities were in the range of 3–50 MBq g^{-1}.

Tertiary T-Labeled Isooctane. A 20-mmol sample of an olefin mixture consisting of 2,2,4-trimethyl-1- and -2-pentene in 10 mL of dry ether was gassed with a stream of dry HCl for about 1 h at about −20 °C. After consumption of the olefins, the mixture was washed with Na_2CO_3 solution and water. It was dried over Na_2SO_4 before the addition of further 40 mL of dry ether and of 0.5 mL of tritiated water. About 2 g of sodium as thin wire was placed into the solution. From time to time some small amounts of water were carefully added up to the complete consumption of the sodium wire (about 2 mL within 48 h). The ether phase was washed with water and dried. After removing the solvent the hydrocarbon was purified by bromination, distillation, and preparative GLC as described above. The procedure gave isooctane with a 60% yield, a 98% GLC purity (before preparative GLC purification), and an exclusive labeling in the desired position.

Primary and Secondary T-Labeled Isooctane. The procedure described above for tertiary T-labeled isooctane was modified in two points: (1) As starting materials pure 2,2,4-trimethyl-1- and -2-pentene were used instead of the olefin mixture. (2) The incorporation of tritium into the molecule took place in the hydrochlorination step instead of the reduction step.

For this purpose the HCl stream passed a mixture of 0.5 mL of tritiated water in 2 mL of dioxane before it reacted with isooctene.

Acknowledgment. Thanks are due to Prof. G. Bach for helpful discussions and Dr. B. Olk for the ^{2}H NMR spectra.

Registry No. DBPO, 94-36-0; Ph$^\bullet$, 2396-01-2; $Br(CH_2)_6CH_3$, 629-04-9; $T(CH_2)_6CH_3$, 3675-58-9; $H_3C(CH_2)_4CHBrCH_3$, 1974-04-5; $H_3C(CH_2)_4CHTCH_3$, 119819-99-7; $H_3CCH_2CHBr(CH_2)_3CH_3$, 1974-05-6; $H_3CCH_2CHT(CH_2)_3CH_3$, 119820-00-7; $H_3C(CH_2)_2CHBr(CH_2)_2CH_3$, 998-93-6; $H_3C(CH_2)_2CHT(CH_2)_2CH_3$, 92204-46-1; $H_3C(CH_2)_6CT(CH_3)_2$, 119820-01-8; $H_3C(CH_2)_6CBr(CH_3)_2$, 119819-98-6; $H_3C(CH_2)_5CHBr(CH_2)_6CH_3$, 74036-97-8; $H_3C(CH_2)_5CHT(CH_2)_6CH_3$, 119820-02-9; $(H_3C(CH_2)_3CBr$, 73908-04-0; $(H_3CCH_2)_3CT$, 119820-03-0; $(H_3CCH_2)_2CBrCH_3$, 25346-31-0; $(H_3CCH_2)_2CTCH_3$, 119820-04-1; $(H_3C)_3CCH_2C(CH_3){=}CH_2$, 107-39-1; $(H_3C)_3CCH_2CH(CH_3)CH_2T$, 119820-05-2; $(H_3C)_3CCH{=}C(CH_3)_2$, 107-40-4; $(H_3C)_3CCHTCH(CH_3)_2$, 119820-06-3; $(H_3C)_3CCH_2CT(CH_3)_2$, 119820-07-4; c-$C_6H_{11}Br$, 108-85-0; c-$C_6H_{11}T$, 3508-33-6; c-$C_6H_{11}CH_2Br$, 2550-36-9; c-$C_6H_{11}CH_2T$, 119820-08-5; c-$C_6H_{10}(Br)CH_3$, 931-77-1; c-$C_6H_{10}(T)CH_3$, 119820-09-6; $H_3C(CH_2)_5CH_3$, 142-82-5; $H_3C(CH_2)_6CH(CH_3)_2$, 871-83-0; $H_3C(CH_2)_{12}CH_3$, 629-59-4; $(H_3CCH_2)_3CH$, 617-78-7; $(H_3CCH_2)_2CHCH_3$, 96-14-0; $(H_3C)_3CCH_2CH(CH_3)_2$, 540-84-1; c-C_6H_{12}, 110-82-7; c-$C_6H_{11}CH_3$, 108-87-2; T_2, 10028-17-8.

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