

# Absolute Rate Constants for Hydrogen Abstraction from Aldehydes and Conformational Studies of the Corresponding Aromatic Acyl Radicals

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**Abstract:** Absolute rate constants for the reactions of *tert*-butoxyl radicals with some organic aldehydes have been measured in solution by using laser flash photolysis techniques. At 297 K, the rate constants are 8.9, 6.8, 1.0, and  $0.05 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for EtCHO,  $\text{C}_6\text{H}_5\text{CHO}$ ,  $\text{Me}_2\text{NCHO}$ , and EtOCHO, respectively. Arrhenius parameters were determined for benzaldehyde. Polar effects are very important in determining the reactivity of organic aldehydes toward *tert*-butoxyl radicals. The EPR spectra are described for a number of furoyl, thenoyl, and pyrrolyl radicals ( $\text{Ar}\dot{\text{C}}\text{O}$ ) which were generated photolytically over a wide range of temperatures. Conformational isomers were detected and their structural assignment obtained from the magnitude of the hyperfine splittings of the ring protons, by comparison with the conformers of the parent aldehydes, and from the solvent dependence.

Aldehydes are known to react with a variety of free radicals to form acyl radicals. Although these are important intermediates in many chemical reactions, absolute rate data regarding their formation from aldehydes by alkoxy radicals are extremely limited. In fact, absolute rate data are restricted to a single gas-phase study of H-atom abstraction by the *tert*-butoxyl radical from formaldehyde and acetaldehyde.<sup>2</sup> In the present work we report a kinetic study of the formation of acyl radicals by the reaction of *tert*-butoxyl radicals with a variety of organic aldehydes in solution, as well as the rates of decay of some acyl radicals, by laser flash photolysis and kinetic EPR spectroscopy, respectively.

The acyl radicals generated by this procedure have been extensively studied in the past by means of EPR spectroscopy, in order to elucidate their structure and conformation.<sup>3-7</sup> Davies and Sutcliffe<sup>7</sup> recently found that the conformational behavior of aliphatic acyl radicals parallels that of the parent aldehydes; they also showed that there is restricted motion around the C-CO bond in some of these radicals. Similarly, the benzoyl radical was shown to experience a restricted rotation around the same bond below 150 K,<sup>3</sup> with a relatively low barrier compared to that of the parent molecule.<sup>8</sup> However, in the present work further studies by EPR and NMR spectroscopies on the conformational properties of the acyl radicals derived from thiophen-, furan-, and pyrrole-carbaldehydes show that the conformer ratio of the radicals is either independent of or dependent on that of the parent molecules according to the value of the rotational barrier in the radical.

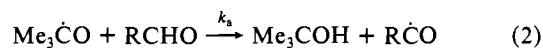
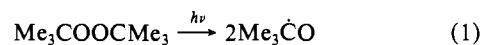
**Table I.** Absolute Rate Constants for the Reaction of *tert*-Butoxyl Radicals with Some Aldehydes at 297 K<sup>a</sup>

substrate	$k_a,^b \text{ M}^{-1} \text{ s}^{-1}$
propionaldehyde	$(8.9 \pm 0.7) \times 10^7$
<i>N,N</i> -dimethylformamide	$(1.0 \pm 0.1) \times 10^7$
ethyl formate	$(5.1 \pm 0.9) \times 10^5$
benzaldehyde	$(6.8 \pm 0.2) \times 10^7$ <sup>c</sup>
perdeuteriobenzaldehyde	$(3.7 \pm 0.1) \times 10^7$
2-furancarbaldehyde	$(3.9 \pm 0.2) \times 10^7$
2-thiophenecarbaldehyde	$(7.5 \pm 0.4) \times 10^7$

<sup>a</sup>  $\pm 2 \text{ K}$ . <sup>b</sup> Error limits represent 95% confidence level. <sup>c</sup> Value derived from the complete kinetic study between 264 and 326 K, not just from the data at this temperature.

## Results

**Laser Flash Photolysis.** In principle this technique allows rate constants to be measured directly by monitoring either the decay of a reagent or the growth of the product of a reaction. However, in our case, transient optical absorptions due to *tert*-butoxyl (reagent) or acyl (product) radicals are too weak to allow detailed kinetic studies,<sup>10,11</sup> particularly if one considers that in order to minimize the occurrence of second-order processes, it is usually necessary to considerably attenuate the excitation dose. For these reasons we preferred to use the technique developed earlier,<sup>12</sup> which makes use of diphenylmethanol as a probe.



In this technique, the kinetics of formation of  $\text{Ph}_2\dot{\text{C}}\text{OH}$  are monitored for a series of samples with a constant concentration of diphenylmethanol and variable concentrations of substrate. The

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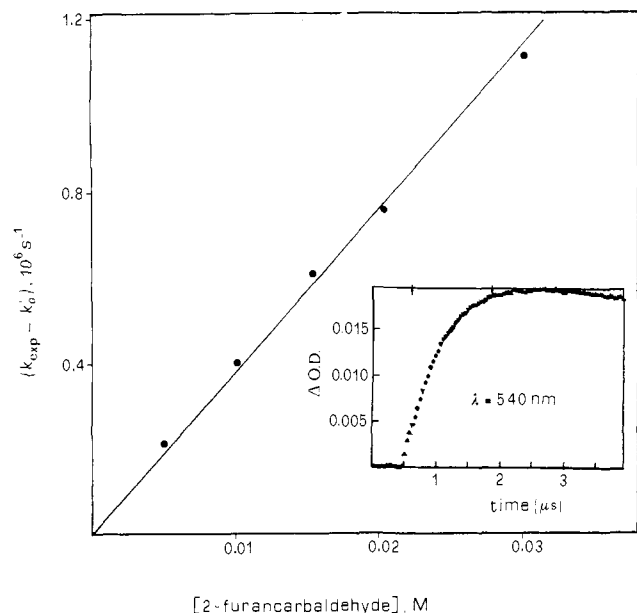
(8) The free energy of activation for the C-CHO rotation in benzaldehyde is 7.7 kcal mol<sup>-1</sup>.

(9) Lunazzi, L.; Macciantelli, D.; Boicelli, A. C. *Tetrahedron Lett.* **1975**, 1205-1206.

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(12) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520-4527. Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49-51.



**Figure 1.** Plot of the experimental rate constant,  $k_{\text{exptl}}$  (corrected for  $k'_0$ ) for the reaction of *tert*-butoxyl and 2-furancarbaldehyde at 298 K. Inset: representative trace monitored at 540 nm for [2-furancarbaldehyde] = 0.02 M. (The section between the arrows corresponds to the points used for kinetic calculations.)

time profiles for the formation of  $\text{Ph}_2\dot{\text{C}}\text{OH}$  (monitored at 540 nm) lead to an experimental pseudo-first-order rate constant,  $k_{\text{exptl}}$ , which is related to the elementary steps of interest according to eq 4, where  $k_0$  is the rate of *tert*-butoxyl decay in the solvent

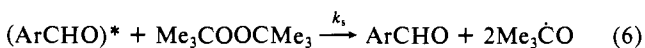
$$k_{\text{exptl}} = k_0 + k_B[\text{Ph}_2\text{CHOH}] + k_a[\text{substrate}] \quad (4)$$

(controlled by hydrogen abstraction and  $\beta$ -scission) and  $k_a$  and  $k_B$  are the rate constants for the reaction of *tert*-butoxyl with the substrate and diphenylmethanol, respectively. Since the concentration of the latter is constant, eq 4 reduces to eq 5.

$$k_{\text{exptl}} = k'_0 + k_a[\text{substrate}] \quad (5)$$

The values of  $k_a$  obtained in this way are absolute rate constants and measure the overall (or molecular) reactivity of the substrate, regardless of the mechanism of the reaction. The results for a number of substrates, containing the  $-\text{CHO}$  group, are summarized in Table I.

In the case of aromatic and heteroaromatic aldehydes the situation is slightly more complex due to the larger absorption at 337 nm.<sup>13</sup> At concentrations which would allow the growth of  $\text{Ph}_2\dot{\text{C}}\text{OH}$  to be easily monitored, we expected a predominant excitation of aromatic aldehydes, leading to interference by its triplet state and a decrease in free radical production. Contrary to expectation, on following normal procedures with aldehyde concentrations of ca. 0.0 to ca. 0.3 M excellent kinetic traces were obtained from which  $k_a$  was readily calculated (see, for example, Figure 1). There can be little doubt that the laser light was largely absorbed by the aromatic aldehydes rather than by the peroxide. Therefore, we propose that aldehyde triplets ( $\text{ArCHO}^*$ ) sensitize the decomposition of the peroxide (eq 6). From a comparison



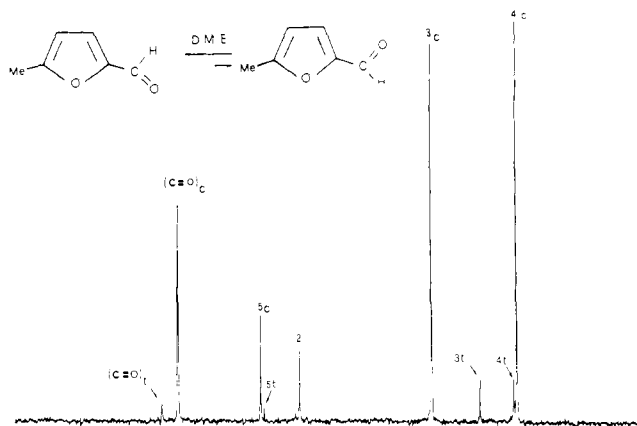
with other sensitizers we estimate that  $k_s$  is ca.  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>14-16</sup>

(13) For example,  $\epsilon_{337}$  are 29, 176, 245, and 346 for propionaldehyde, benzaldehyde, 2-furancarbaldehyde, and 2-thiophenecarbaldehyde, respectively.

(14) Scaiano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640-645.

(15) Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5119-5123.

(16) In studies of free radicals it has sometimes been found useful to sensitize the decomposition of di-*tert*-butyl peroxide, see: Griller, D.; Ingold, K. U.; Scaiano, J. C. *J. Magn. Reson.* **1980**, *38*, 169-171.



**Figure 2.**  $^{13}\text{C}$  NMR spectrum (25.16 MHz) of 5-methylfuran-2-carbaldehyde (downfield region) taken in dimethyl ether at 173 K. The lines marked with a "c" belong to the major conformer syn (or cis) and those marked with a "t" belong to the minor conformer anti (or trans).

This reaction makes the absorption of light by  $\text{ArCHO}$  formally equivalent to absorption by the peroxide.

For benzaldehyde the temperature dependence for the reaction with *tert*-butoxyl was examined in 1:2 (v/v) benzene:di-*tert*-butyl peroxide. Between 264 and 326 K the results could be represented by

$$\log(k_a/\text{M}^{-1} \text{ s}^{-1}) = (8.76 \pm 0.08) - (1.26 \pm 0.11)/\theta$$

where  $\theta = 2.3RT \text{ kcal mol}^{-1}$  and the errors correspond to 95% confidence limits.

**NMR Studies.** The  $^{13}\text{C}$  NMR spectra (in dimethyl ether) and the H-1 NMR spectra (in carbon disulfide) of 5-methyl-2-furancarbaldehyde were recorded as a function of temperature. Below 220 K some of the lines broaden, owing to the exchange between the O,O-syn and O,O-anti conformers. At 173 K in dimethyl ether two sets of signals in a 90:10 ratio were eventually detected (Figure 2), the more intense being that corresponding to the O,O-syn conformer.<sup>17</sup> The ratio is equal to that reported<sup>18,19</sup> for 2-furancarbaldehyde in the same solvent and temperature, thus indicating that the presence of a methyl in position 5 does not affect the conformer ratio in polar solvents such as dimethyl ether. In apolar solvents, such as carbon disulfide, the conformer ratio of the unsubstituted 2-furancarbaldehyde is known<sup>20</sup> to be 53:47 (at 183 K). On the other hand, our results for 5-methyl-2-furancarbaldehyde in carbon disulfide show that the ratio is completely different (75:25 at 173 K). The introduction of a methyl group in position 5 thus modifies the conformer ratio of 2-furancarbaldehyde in an apolar solvent. As a consequence the O,O-syn conformer of the 5-methyl derivative is by far the more stable of the two possible conformers, whatever the polarity of the solvent employed.

The  $^{13}\text{C}$  NMR spectra of 2- and 3-thiophenecarbaldehyde displayed, below room temperature, line-broadening effects due to exchange between a pair of conformers. Below 173 K two different spectra were eventually detected for the syn and anti conformers: the amounts of the major conformers were found, in both isomers (2- and 3-thiophenecarbaldehyde), to be greater than 95%.<sup>21</sup> The free energy of activation ( $\Delta G^\ddagger$ ) for the rotation of the  $-\text{CHO}$  moiety was found to be 10.15 and 8.15  $\text{kcal mol}^{-1}$  for 2- and 3-thiophenecarbaldehyde, respectively,<sup>22</sup> values close

(17) The assignment results from the knowledge that the  $^{13}\text{C}$  chemical shift of a C-3 syn to carbonyl is upfield with respect to that of a C-3 anti to carbonyl.<sup>9,18</sup>

(18) Roques, B. P.; Combrisson, S.; Wehrli, F. *Tetrahedron Lett.* **1975**, 1047-1050.

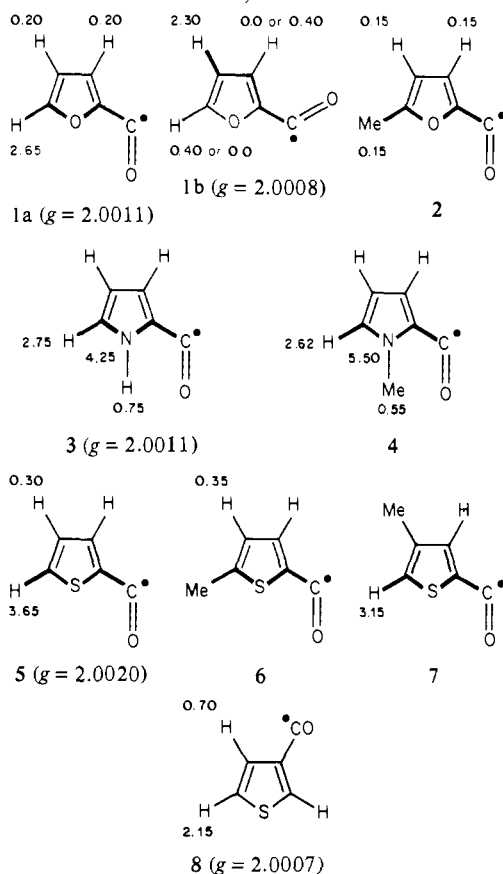
(19) Dahlqvist, K. I.; Fors n, S. *J. Phys. Chem.* **1965**, *69*, 4062-4071.

(20) Chadwick, D. J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 451-452.

(21) The same criterion of ref 17 indicates that 2-thiophenecarbaldehyde essentially adopts the S,O-syn and the 3-thiophenecarbaldehyde the S,O-anti conformation.<sup>22</sup> These conclusions also agree with those obtained by using different experimental methods.<sup>23</sup>

(22) Lunazzi, L.; Placucci, G.; Chatgililoglu, C.; Macciantelli, D. *J. Chem. Soc., Perkin Trans. 2* **1983**, 819-822.

Chart I. EPR Parameters of Heteroaromatic Acyl Radicals Observed on Photolysis of the Corresponding Aldehydes in the Presence of Di-*tert*-butyl Peroxide in Cyclopropane Solutions at 173 K (hfs in Gauss)



to those measured for 2-furancarbaldehyde and benzaldehyde (10.9 and 7.7 kcal mol<sup>-1</sup>, respectively<sup>19,9</sup>).

**EPR Studies.** Acyl radicals were generated by photolysis of di-*tert*-butyl peroxide (*t*-BuOOBu-*t*) and aromatic aldehydes in cyclopropane. In the absence of *t*-BuOOBu-*t*, no radicals were observed,<sup>24</sup> thus suggesting a relatively low reactivity of H-atom abstraction by aldehyde triplets (ArCHO)\*. The same results indicate that the process of energy transfer from the excited state to di-*tert*-butyl peroxide must be the key step in the formation of aromatic acyl radicals. The EPR data for a number of heteroaromatic acyl radicals (1–8) are shown in Chart I; the assignments of the hyperfine splittings and of the preferred conformations will be justified in the analysis presented in the Discussion.

In contrast to the other spectra, that of the 2-furoyl radical (1) displays two groups of lines due to the presence of a pair of conformers (1a and 1b), their relative ratio depending upon the polarity of the solvent employed: in cyclopropane and dimethyl ether the ratio is ca. 60:40 (Figure 3) and ca. 80:20, respectively, at 173 K.

The spectrum of the 3-thenoyl radical (8), unlike those of all the other radicals investigated, displays alternating line-width effects, which are temperature dependent. We attributed this phenomenon, which is similar to that reported<sup>3</sup> for the benzoyl radical, to restricted rotation around the C–CO bond (see Dis-

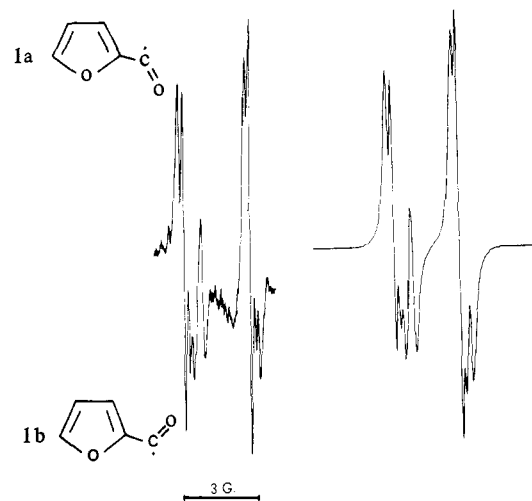
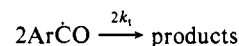


Figure 3. Experimental (left) and computer-simulated spectra (right) of radicals 1a and 1b in cyclopropane at 173 K. The simulated spectrum was obtained with the  $a_H$  and  $g$  values listed in Table II and with a conformer ratio of 60:40.

ussion). As in the case of the benzoyl radical we could not reach a temperature sufficiently low to allow the detection of separate lines for the individual conformers. However, from the theory of line broadening it appears that the corresponding  $\Delta G^\ddagger$  value is certainly lower than 4 kcal mol<sup>-1</sup> for both benzoyl and 3-thenoyl radicals.

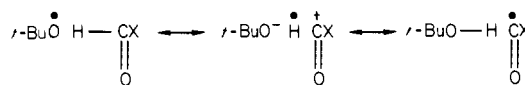
The bimolecular termination rate constants ( $2k_t$ ) were also measured by time-resolved EPR<sup>26</sup> for some of the radicals investigated, using a pulsed nitrogen laser as the light source for generating the radicals. The  $2k_t$  values for the termination reaction



obtained for 1, 5, and the benzoyl radical are respectively  $(3.5 \pm 1.5) \times 10^9$ ,  $(3.0 \pm 1.5) \times 10^9$ , and  $(4.0 \pm 1.0) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> at 203 K.

## Discussion

**Kinetics.** The similarity in the  $k_a$  values for CH<sub>3</sub>CH<sub>2</sub>CHO and C<sub>6</sub>H<sub>5</sub>CHO was not unexpected since both alkylacyls and arylacyls have been shown by EPR spectroscopy to be  $\sigma$ -radicals.<sup>3,4,7,27</sup> Since in such  $\sigma$ -radicals there can be little or no delocalization of the unpaired electron, even when there is a neighboring aromatic ring, the bond strengths of the parent aldehydes,  $D[\text{RCO-H}]$ , are virtually independent of the nature of the R group.<sup>28</sup> However, the rates are drastically affected by the introduction of a stronger electron-withdrawing substituent instead of alkyl or aryl, e.g., amino in formamides or alkoxy in formates (see Table I). We attribute this decrease in the rate constants to the greater importance of the polar contribution to the transition state for propionaldehyde H-atom abstraction with respect to hydrogen abstraction from *N,N*-dimethylformamide or ethyl formate, viz.,<sup>34,35</sup>



(23) Abraham, R. J.; Chadwick, D. J.; Sancassan, F. A. E. G. *Tetrahedron* 1982, 38, 3245–3254. Roques, B. P.; Combrisson, S. *Can. J. Chem.* 1973, 51, 573–581. Lunazzi, L.; Veracini, C. A. *J. Chem. Soc., Perkin Trans. 2* 1972, 1739–1741. Roques, B. P.; Fourniè-Zaluski, M. C. *Org. Magn. Reson.* 1971, 3, 305–312. Roques, B. P.; Combrisson, S.; Riche, C.; Pascard-Billy, C. *Tetrahedron* 1970, 26, 3555–3567. Fourniè-Zaluski, M. C.; Roques, B. *Tetrahedron Lett.* 1970, 4909–4912. Abraham, R. J.; Chadwick, D. J.; Sancassan, F. *Tetrahedron* 1982, 1485–1491.

(24) No EPR evidence was obtained for the  $\alpha$ -hydroxybenzyl radical which would be formed by photoreduction of benzaldehyde.<sup>25</sup>

(25) Wilson, R. *J. Chem. Soc. B* 1968, 84–90.

(26) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* 1980, 13, 193–200.

(27) Paul, H.; Fischer, H. *Helv. Chim. Acta* 1973, 56, 1575–1594.

(28) The C–H bond strengths in aldehydes are  $87.0 \pm 1.0$ ,  $86.0 \pm 0.8$ ,  $87.4 \pm 1.0$ ,  $86.9 \pm 1.0$ , and  $91.0 \pm 2.0$  kcal mol<sup>-1</sup> for HCHO,<sup>29</sup> MeCHO,<sup>30</sup> EtCHO,<sup>31</sup> C<sub>6</sub>H<sub>5</sub>CHO,<sup>32</sup> and CF<sub>3</sub>CHO,<sup>33</sup> respectively.

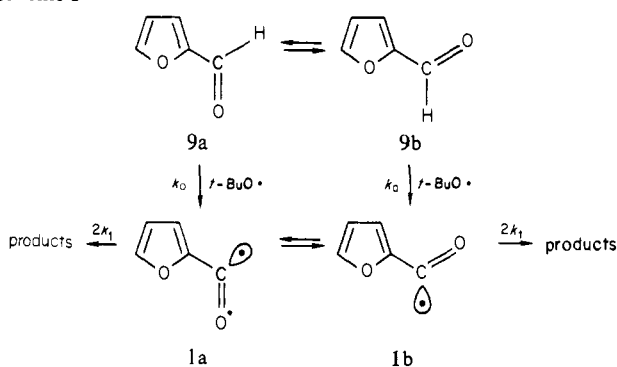
(29) Walsh, R.; Benson, S. W. *J. Am. Chem. Soc.* 1966, 88, 4570–4575.

(30) Devore, J. A.; O'Neal, H. E. *J. Phys. Chem.* 1969, 73, 2644–2648.

(31) Watkins, K. W.; Thompson, W. W. *Int. J. Chem. Kinet.* 1973, 5, 791–803.

(32) Solly, R. K.; Benson, S. W. *J. Am. Chem. Soc.* 1971, 93, 1592–1595.

Scheme I



Furthermore, the small differences observed in the rate constants for the various carbon-substituted aldehydes, e.g., 3.9, 6.8, 7.5, and  $8.9 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  for 2-furancarbaldehyde, benzaldehyde, 2-thiophenecarbaldehyde, and propionaldehyde, respectively, are nevertheless significant. In fact such changes could be due to different polar contributions to the transition state as the 2-furan group has a greater electron-withdrawing power than the benzene or the 2-thiophene groups which, in turn, have more electron-withdrawing power than the ethyl group.<sup>36,37</sup>

The Arrhenius parameters obtained for hydrogen abstraction from PhCHO by *tert*-butoxyls show a "normal" pre-exponential factor<sup>38</sup> while the activation energy, 1.26 kcal/mol, is appreciably lower than the values measured for hydrocarbons.<sup>39</sup> Replacement of the aldehyde hydrogen with deuterium yields a kinetic isotope effect,  $k_{\text{H}}/k_{\text{D}} = 1.8 \pm 0.1$ . Relative rate constants for H-atom abstraction from a number of substituted benzaldehydes have been reported recently,<sup>41</sup> and a  $\rho^+$  value of  $-0.32$  was rationalized in terms of a polar contribution to the transition state. Our data indicate that these reactions (at 403 K) have rate constants in a range close to the diffusion-controlled limit (ca.  $10^8 \text{ M}^{-1}\text{s}^{-1}$ ).

Our laser flash photolysis results are in excellent agreement with the competitive studies of Walling and Mintz,<sup>42</sup> who obtained a relative rate constant of  $1.2 \pm 0.20$  at 273 K for H-atom abstraction from the  $\text{CH}_3\text{CHO}/\text{C}_6\text{H}_5\text{CHO}$  system by *tert*-butoxyl radicals, which is to be compared with the ratio  $1.3 \pm 0.15$  at 297 K derived from the data of Table I. However, our rate constant for propionaldehyde in solution ( $8.9 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  at 297 K) is considerably higher than the gas-phase values for HCHO and  $\text{CH}_3\text{CHO}$  (viz., 2.0 and  $1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ , respectively, at 399 K).<sup>2</sup> Furthermore, the Arrhenius parameters for formaldehyde are somewhat different from those we obtained for benzaldehyde.<sup>43</sup> Although a phase and/or a specific solvent effect cannot be ruled

out as an explanation for these differences, it does seem rather unlikely. We therefore attribute these discrepancies to the approximations employed in the kinetic analysis of the data obtained in the gas phase.

**Conformational Analysis.** The conformation of the radicals investigated will be dependent upon that of the precursor aldehyde molecules, provided that the rates of radical decay,  $2k_1$ , are greater than the rates of the interconversion between the two conformer radicals (see Scheme I).

The existence of two rotational conformers O,O-syn (**9a**) and O,O-anti (**9b**) in 2-furancarbaldehyde is well documented from NMR experiments,<sup>18,20,44</sup> and the interconversion rates have been measured,<sup>45</sup> the low-temperature NMR measurements indicated that the O,O-syn conformer (**9a**) is the more stable and that the conformer ratio (**9a:9b**) is strongly dependent upon the polarity of the solvent. These observations offer a unique opportunity of investigating the relationship between the conformational behavior of the arylacyl radicals with respect to the parent aldehydes. In fact, when we ran the EPR spectra of the 2-furoyl radical in cyclopropane and in dimethyl ether, the conformer ratio changed from ca. 60:40 to ca. 80:20 at 173 K, whereas in the case of 5-methyl-2-furoyl only one conformer was observed in both solvents, within the accuracy obtainable with the not-too-favorable signal-to-noise ratio. These values match the conformer ratio of the parent molecules remarkably well, indicating that the radical conformers **1a** and **1b** do not reach, apparently, a thermodynamic equilibrium of their own but that the ratio depends upon the thermodynamic equilibrium of the parent molecule (see Scheme I). Consequently, the conformation O,O-syn (**1a**) is assigned to the more-abundant and the O,O-anti (**1b**) to the less-abundant species. In the case of the 5-methyl derivative where, within the limits of the measurements, only the major conformer was observed in the EPR spectrum, the O,O-syn structure (**2**) was assigned to it. As in the case of **2**, the spectra of the other radicals (**3-7**) also displayed symmetric lines, thus indicating that they most likely exist as single conformers. The corresponding parent aldehydes are known to adopt, essentially, a single conformation at the low temperatures required to observe the EPR spectra and, since the conformation of these aldehydes was found to be syn<sup>22,23,46</sup> the same conformation was also assigned to the corresponding acyl radicals **3-7**.

On the contrary, radical **8** interconverts between two conformers of comparable amounts, thus reaching its own thermodynamic equilibrium, with a conformer ratio which is different from that of its parent aldehyde. The latter, in fact, has been shown to exist, at the temperature of our EPR experiments, mainly in the anti form (93–97%).<sup>22</sup> These observations lead to the conclusion that there is a parallel behavior between the rotational barrier in the acyl radical and in the parent aldehyde. We suggest that when the molecule has a barrier lower than about 9 kcal mol<sup>-1</sup> (as in benzaldehyde<sup>8</sup> or 3-thiophenecarbaldehyde<sup>22</sup>) the corresponding acyl radicals have barriers *too low* to be determined by EPR. When the molecule has a barrier higher than 10 kcal mol<sup>-1</sup> (as in 2-furancarbaldehyde<sup>19</sup>) the barrier of the corresponding acyl radical **1** has a barrier *too high* to be determined under our experimental conditions. Consequently, we believe that the acyl radicals **1-7**, whose parent aldehydes have relatively high rotational barriers, decay faster than they interconvert so that their conformational ratio is mainly determined by that of the parent molecule. This allows us to transfer the assignment of the con-

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(34) For a general discussion of polar effects in radical reactions, see: Minisci, F.; Citterio, A. *Adv. Free-Radical Chem.* **1980**, 6, 65–153. Russell, G. A. *Free Radicals* **1973**, 6, 275–331.

(35) In addition to the Et-CO radical, H-atom abstraction from ethyl formate (EtO-CHO) also produces at least two radicals of the type Me-CH-X. One of these (Me-CH-OCHO) has been reported to occur also when OH is the abstractor.<sup>5</sup> Therefore, since laser flash photolysis, as we have used it, measures the average rate constant of any process occurring in the system, the value of Table I for ethyl formate is *not* a precise value of the rate constant of H-atom abstraction from CHO. Nonetheless, since the intensity of the radical Et-CO, as measured by EPR, is *lower* than that of the other radicals, the corresponding abstraction rate is even lower than the measured value of Table I. The trend indicating a decreasing rate with increasing electronegativity of the substituents is, accordingly, confirmed.

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(38) Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976.

(39) The activation energies for H-atom abstraction from cyclopentane and norbornane by *tert*-butoxyl radicals are 3.5 and 2.9 kcal mol<sup>-1</sup>, respectively.<sup>40</sup>

(40) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, 104, 5106–5108.

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(42) Walling, C.; Mintz, M. J. *J. Am. Chem. Soc.* **1967**, 89, 1515–1519.

(43) The CO-H bond strengths for formaldehyde and benzaldehyde are the same (see ref 28).

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(45) The order of magnitude of the lifetime for the O,O-syn conformer of 2-furancarbaldehyde (**9a**) is  $10^{-1}$  s (at 203 K)<sup>19</sup> while the lifetimes of radicals **1a** and **1b** are ca.  $10^{-3}$  s at the same temperature. The 2-furoyl radicals **1a** and **1b** thus decay at least 100 times faster than the conformer of the parent molecule interconversion. At temperatures lower than 203 K the gap between the lifetimes is even larger, since that for the interconversion further increases (8 s at 158 K)<sup>19</sup> while that for the termination processes remains essentially the same.

(46) Roques, B. P.; Jaureguierry, C.; Fourniè-Zaluski, M. C.; Combrisson, S. *Tetrahedron Lett.* **1971**, 2693–2696. Jaureguierry, C.; Fourniè-Zaluski, M. C.; Roques, B.; Combrisson, S. *Org. Magn. Reson.* **1973**, 5, 165–168.

formers from the molecule to the radical.

Corroborative evidence for our conclusions is based on the observation of the hydrogen hyperfine splitting (hfs) constants in the light of the W empirical rule. It has been in fact recognized that in  $\sigma$ -radicals the largest hfs are expected at the positions corresponding to the extreme of a zigzag (or W) chain of bonds, having the orbital of the unpaired electron at the other extreme.<sup>47</sup> In the case of the S,O-syn conformer of 2-thenoyl radical, **5**, this rule predicts the largest hfs to be at position 5, in agreement with the experimental assignment obtained after methyl substitution (see radicals **6** and **7** in Chart I). Similarly, in the O,O-syn conformer of the 2-furoyl radical, **1a**, the largest hfs comes from position 5 (see the 5-methyl-substituted radical **2**), again in agreement with the zigzag rule; it is therefore reasonable to assume<sup>51</sup> the largest hfsc to be at position 4 in the O,O-anti conformer, **1b**.

### Experimental Section

The aldehydes used in this work were purified by distillation immediately before the experiments: without this precaution nonreproducible results were obtained.

Di-*tert*-butyl peroxide was passed through alumina so as to remove traces of di-*tert*-butyl hydroperoxide.

The kinetics of H-atom abstraction were performed by using a laser flash photolysis apparatus, equipped with optical detection with a pulsed Molecron nitrogen laser (337.1 nm, 8 ns, 10 mJ). This apparatus and associated experimental procedures have been described elsewhere.<sup>52</sup>

(47) See, e.g., benzoyl,<sup>3</sup> arylidiazanyl,<sup>48</sup> arenesulfonyl,<sup>49</sup> and sulfuranyl<sup>50</sup> radicals.

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(51) INDO calculations carried out for the S,O-anti conformation of the 2-thenoyl radical predict the largest hydrogen splitting to be at the position which obeys the zigzag rule, i.e., H-4 for this conformation (Wiffen, J. T. Ph.D. Thesis, 1974, University of Sussex, U.K.). The authors thank Dr. A. Hudson, Brighton, U.K., for this information.

The solvent used in the laser flash photolysis experiments was a 1:2 (v/v) mixture of benzene and di-*tert*-butyl peroxide; all the samples were carefully deoxygenated.

EPR spectra were recorded on a Varian E-104 instrument; the samples were photolyzed directly in the cavity of the spectrometer with a 500-W mercury lamp as irradiating source. Measurement of the bimolecular decay kinetics was carried out by generating the radicals with the repetitive pulses of the same Molecron nitrogen laser. The time profile of the growth and decay of the radical signal (time-resolved EPR spectroscopy) was obtained by feeding the unfiltered output of the EPR spectrometer into a Nicolet 1170 signal averager. Radical concentrations were measured with a method that has been described previously.<sup>26</sup>

The NMR spectra were recorded with a Varian XL-100 instrument equipped with a thermocouple inserted in the probe before or after each experiment. The <sup>13</sup>C spectra (25.16 MHz) were obtained in the FT mode (10-mm tubes) on an external Fluorine lock device. The H-1 spectra (100 MHz) were obtained in the FT mode with use of coaxial 5-mm tubes; deuterated acetone in the inner tube provided the signal for the internal deuterium lock.

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**Registry No.** **1a**, 83323-06-2; **2**, 90866-67-4; **3**, 90866-68-5; **4**, 90866-69-6; **5**, 90866-70-9; **6**, 90866-71-0; **7**, 90866-72-1; **8**, 90866-73-2; *t*-BuO•, 3141-58-0; CH<sub>3</sub>CH<sub>2</sub>CHO, 123-38-6; HC(O)NMe<sub>2</sub>, 68-12-2; HC(O)OEt, 109-94-4; PhCHO, 100-52-7; perdeuteriobenzaldehyde, 17901-93-8; 2-furancarboxaldehyde, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3.

**Supplementary Material Available:** Tables giving detailed kinetic data (11 pages). Ordering information is given on any current masthead page.

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## MNDO Studies of the Didehydrodiazines<sup>1</sup>

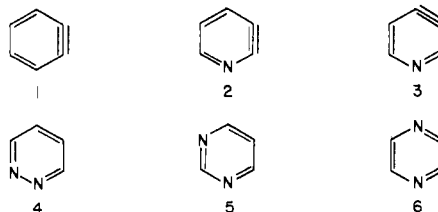
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**Abstract:** MNDO calculations are reported for all the didehydro derivatives of pyridazine, pyrimidine, and pyrazine, and for their possible modes of rearrangement.

Like the more familiar didehydroaromatics, benzyne (**1**) and the didehydropyridines (**2** and **3**), didehydro derivatives of the three diazines (pyridazine (**4**), pyrimidine (**5**), and pyrazine (**6**)) have been postulated as intermediates in a number of reactions.<sup>2-4</sup> The evidence for their intervention is, however, often inconclusive, as is so often the case for reactive species postulated as intermediates in reactions, because it is usually possible to explain the formation of the observed products in other ways.

This is a situation where theoretical calculations can be very useful. While no current theoretical procedure is accurate and



reliable enough to establish the existence of such a species, calculations of this kind may add productively to the body of evidence for it and may also suggest useful avenues of experimental enquiry. Indeed, MINDO/3<sup>5</sup> and MNDO<sup>6</sup> calculations for the dehydro-

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