Arrival Time Distributions in High Pressure Mass Spectrometry. I. Residence Times of Reactant Ions in Chemical Ionization and the Measurement of Reaction Rate Constants[1]

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Abstract: A method for the determination of arrival time distributions in high pressure mass spectrometry (0.5–3 Torr) is described. It employs a pulsed electron gun and time-of-flight analysis of reactant ions using nuclear instrumentation and delayed coincident individual ion detection. Arrival time distributions of CH_5^+ and $C_2H_5^+$ are presented, and mean residence times calculated from the first moments of these curves are shown to be substantially less than those calculated from idealized Langevin drift theory commonly employed to estimate this quantity. The change in the arrival time distribution of methane ion when small concentrations of methane are added to helium is used to evaluate the total rate constant of methane ion reaction with methane as $1.00 \pm 0.08 \times 10^{-9}$ cc sec^{-1}. It is shown that the simple technique employed for rate constant measurement gives excellent reproducibility and an accuracy which is primarily limited by the ability to assess pressure in the reaction region.

Chemical ionization[2] has become an important tool in analytical chemistry.[3] Recently attention has been focused on the possibility of measuring ion–molecule reaction rate constants under conditions of chemical ionization,[4,5] and the approach has been extended to measure ionic equilibria.[6–8] Results have not always been in agreement with each other,[4,5] and heats of reaction derived from such measurements[6] are not always consistent with those obtained by other methods.[9]

The ion source used in chemical ionization studies is essentially a conventional Nier electron impact source with greatly reduced electron entrance and ion exit slits, permitting the achievement of pressures on the order of 1–3 Torr in the source. A weak draw-out or repeller electric field is superimposed. The electron energy is typically on the order of 160–250 eV to improve penetration into the chamber, and the beam is centered approximately 3–10 mm from the ion exit slit. In order to carry out quantitative determinations of first- and second-order rate constants it is necessary to know residence time of ions in the source under these conditions.[4,5] Similarly, residence time is an important parameter in the assessment of the applicability of equilibrium considerations.[7] These times are calculated from idealized ion drift considerations originally developed by Langevin[10] and summarized by McDaniel.[11] However, it is known that such calculated residence times can be substantially in error even under idealized drift conditions.[11,12] We have therefore constructed a pulsed high-pressure ionization source and report here on its use for the determination of ion residence times in chemical ionization and for the rapid and accurate determination of ion–molecule reaction rate constants.

Experimental Section

The high-pressure ion source was constructed by replacing the source block and draw-out slits of a commercial Varian-MAT CH-4, type AN-4B ion source. The revised block has an electron entrance slit of 0.025 × 2.0 mm, while the electron trap is tightly mounted against the flange using a 1-mm Teflon sheet as an insulator. The single draw-out plate contains an ion exit slit of 0.05 × 5.0 mm and is located 7.0 mm from the electron beam and 7.6 mm from the rear wall of the chamber. A 4-in. Edwards pumping system is used to evacuate the region surrounding the ion source, maintaining a pressure of 1 mTorr or less at an ion source pressure of 3 Torr. The source region is connected to the analyzer only through a skimmer throttling tube approximately 5 mm below the beam definining slit. Pressure in the analyzer section did not exceed 0.05 mTorr.

The gas introduction system consists of two 5-l. reservoirs and a 1-l. reservoir. Either of the former and the latter can be opened to the ion chamber *via* Granville–Phillips metering needle valves. Pressure in the ion source is measured with an MKS Baratron capacitance manometer. The sensing side of this manometer is connected to a separate port of the ion source located at right angles to the electron beam and the gas inlet. The pressure gauge was calibrated with an average deviation from the mean of 4% using a trapped McLeod gauge.

The electron gun was pulsed by unblocking a biased 85 line per centimeter tungsten screen (90% transparent) between the rhenium filament and the entrance slit using a 50-nsec pulse from a Hewlett-Packard Model 214A pulse generator. The trigger pulse from the generator also started the voltage ramp of a time-to-pulse height converter (W. H. Johnston Labs). The electron multiplier ion detector output was coupled directly into an amplifier–discriminator and pulse shaper (W. H. Johnston Labs), whose output terminated the voltage ramp of the time-to-pulse height converter, creating a pulse whose height is proportional to flight time. Pulses were sorted on a TMC Model 401B 400 channel pulse height analyzer whose output was either recorded on a Hewlett-Packard Model 2D-2 X-Y recorder or on a Hewlett-Packard Model 500 digital recorder. The experimental arrangement is shown in Figure 1, and a schematic event sequence is shown in Figure 2.

The electron pulse width at the screen was measured using a Tektronix Model 564 oscilloscope with 3S1 and 3T77A plug-ins and showed some broadening to *ca.* 100 nsec FWHM. Arrival time distributions are also greatly affected by the electron beam spread in the ionization region; this was assessed approximately

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[1] Presented in part at the 19th Annual Meeting on Mass Spectrometry and Allied Topics, Atlanta, Ga., May 1971.

[2] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 1621 (1966).

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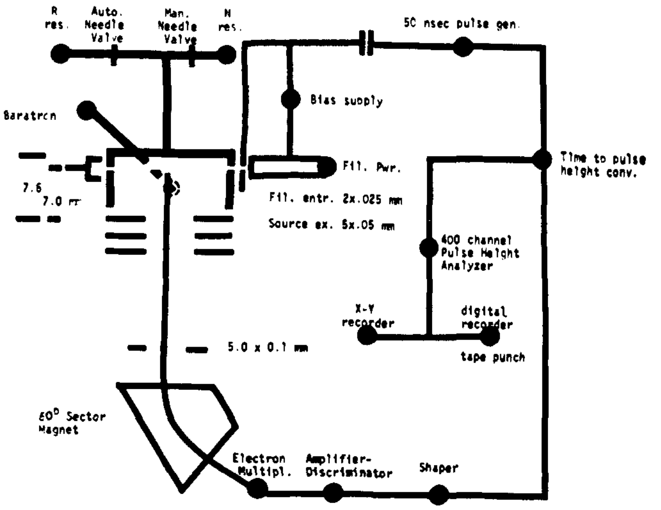

Figure 1. Schematic of experimental arrangement for arrival time measurements.

by evaluating the arrival time distribution of CH_4^+ ion from methane at the lowest pressure where sufficient count rates could be obtained (*ca.* 1 mTorr); the distribution had a width of *ca.* 0.5 msec at half maximum.

Results and Discussion

A. Residence Times of CH_5^+ and $C_2H_5^+$ Ions in Methane. The drift velocity of ions in gases[11] is related to applied field strength E (V/cm) by the relationship

$$v_d = KE \qquad \text{(I)}$$

where K is the mobility, which is dependent on pressure P (Torr) and temperature T (°K) but, at least at low values of E/P, is independent of E. The reduced mobility K^0 (at 0° and 760 Torr) is obtained by the relationship

$$K^0 = K(P/760)(273/T) \qquad \text{(II)}$$

This quantity is also directly accessible from ion drift theory and is given by

$$K^0{}_{\text{theor}} = 35.9/(\alpha\mu)^{1/2} \qquad \text{(III)}$$

where α is the polarizability in atomic units (0.053 nm) and μ the reduced mass also in atomic units. Equation III applies for slow drift conditions when ion mobility is determined only by the $1/r^4$ potential; the ion energy distribution then reasonably approximates a Maxwell–Boltzman function. Moreover reaction between ions and the drift gas must not occur. The theoretical residence time, t_{theor}, is therefore readily calculated from the expression

$$t_{\text{theor}} = (L/v_d) = (L/E)(P/T)\sqrt{\alpha\mu} \times 10^{-2}\ \text{sec} \qquad \text{(IV)}$$

where L is the drift length of the ion in centimeters and is usually taken to be the distance between electron beam and ion source exit slit.

There are four limitations associated with the application of this equation to the calculation of residence times in chemical ionization sources.

1. Instrumental factors causing unequal sampling of the arrival time distribution and the dependence of this factor on the diffusion coefficient D or on ion mass.

2. The questionable reliability of eq IV under conditions where ion drift is slow even when experimental conditions are well defined. Differences between experimental and calculated diffusion coefficients involving factors up to 10 have been reported.[11,12]

3. The effect of details of the transport process such as ion–molecule reactions, charge transfer, proton transfer, and other metathetical reactions on the momentum transfer cross section.

4. Poorly defined experimental conditions such as pressure, electrical fields, etc. These complications will introduce relatively minor, consistent errors which should not affect relative measurements.

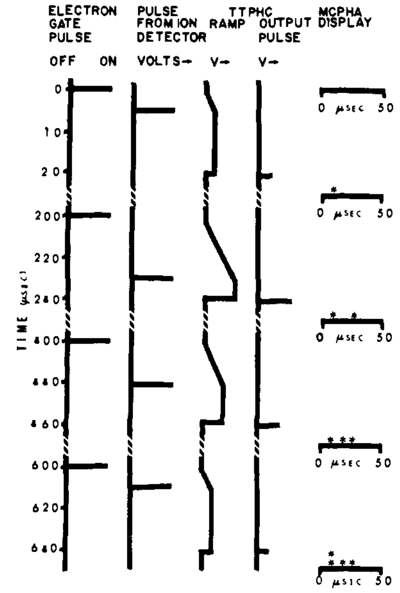

Figure 2. Representative event sequence showing electron gate pulse at 5 kc repetition frequency; pulse created by arrival of ion at the detector after shaping, behavior of the voltage ramp of the time to pulse height converter (TTPHC), the output pulse of that device, and the display which would be visible on the multichannel pulse height analyzer (MCPHA). The vertical displacement of the MCPHA represents the number of events which have occurred within a given time (pulse height) channel. Accumulation is typically for several minutes. In reality, there are a large number of gate pulses which are not followed by ion termination pulses.

In this paper we are chiefly concerned with the first two problem areas. The idealized drift equations are based on complete collection of all ions, corresponding to total ionization measurements. The small ion sampling aperture or ion exit slit in chemical ionization sources discriminates against the observation of ions produced at longer residence times. It can be shown,[13] by consideration of a point source of ion origin and solution of the transport equation[11,14] in cylindrical coordinates, that the fraction of the ions which reach the exit slit plane and pass through the sampling orifice may vary as strongly as $1/Dt$. Experimental ion arrival time distributions span nearly an order of magnitude in time. Time discrimination could therefore be substantial.

The quantity measured in our experiment is an arrival time distribution which includes the transit time through the acceleration and mass analysis regions of the mass spectrometer beyond the ion source exit aperture, as well as the small delays in the electron multiplier and electronics. The totality of these transit times can

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Table I. Diffusion Properties of CH_4^+ and $C_2H_5^+$ Ions in Methane at 440 ± 5°K

Ion	$P(CH_4)$, Torr	E/P, V cm^{-1} Torr^{-1}	τ,[a] µsec	$K_{1atm, 0°}$, cm^2 V^{-1} sec^{-1}	$D_{1atm, 0°}$, (cm^2 sec^{-1}) × 10^2	Nc[b]
CH_5^+	0.670	15.9	20.57	1.75	4.10	302
	0.683	13.5	24.50	1.73	4.05	366
	0.616	12.9	25.68	1.73	4.05	346
	0.680	10.1	33.10	1.71	4.02	493
	0.700	7.1	40.97	1.81	4.25	628
				Av 1.75 ± 0.03	4.16 ± 0.06	
				Theor value 2.92	6.98	
$C_2H_5^+$	0.620	17.2	18.61	1.78	4.18	253
	0.674	14.1	22.82	1.77	4.17	337
	0.567	13.7	23.97	1.75	4.08	298
	0.732	9.3	33.50	1.84	4.32	537
	0.713	7.6	48.00	1.55	3.65	750
				Av 1.74 ± 0.07	4.08 ± 0.16	
				Theor value 2.62	6.15	

[a] Mean experimental residence time. [b] Number of collisions with methane an ion experiences during its mean residence time in the source assuming $k_{collision} = 10^{-9}$ cc sec^{-1}.

be evaluated by changing the field strength in the ion source while examining the flight time of a primary ion at low pressures. Since a draw-out field is used and the ion origin is near the back plate, terminal ion energy in the transit region is essentially unaffected by draw-out field in the absence of ion–molecule reactions. The mean residence time $\bar{t}$ should vary as $(V_{draw\text{-}out})^{-1/2}$. The intercept of a plot of $\bar{t}$ vs. $V^{-1/2}$ therefore gives the transit time. This is demonstrated for CH_4^+ ion in Figure 3. Transit times for ions of other masses can then be calculated from the empirical relationship $t_{transit} = 1.58\sqrt{m/e}$ µsec.

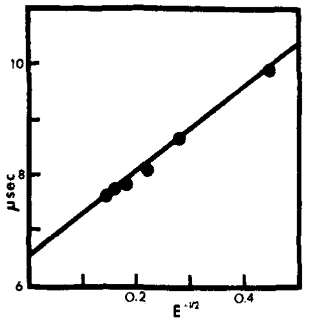

Figure 3. Evaluation of transit time for CH_4^+ ion.

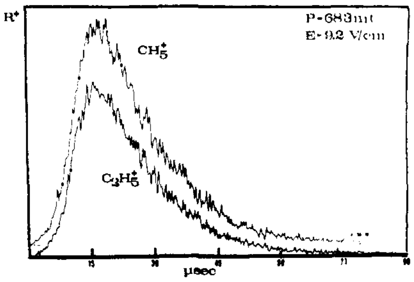

Figure 4. Arrival time distributions of CH_5^+ and $C_2H_5^+$ ions at a source pressure of 683 mTorr and a field strength of 9.2 V/cm; T = 443°K.

Experimentally observed residence time distributions for CH_5^+ and $C_2H_5^+$ ions in methane are shown in Figure 4. Mean arrival times for these ions were calculated at various values of E/P from the first moments of these curves; these in turn yielded $\bar{V}_d = L/\bar{t}$. This formulation is not entirely correct but is thought not to introduce a serious error[15] and is employed commonly.[16] Figure 5 demonstrates that drift velocities calculated in this manner are a linear function of E/P as required for low-field drift conditions. The calculations of reduced mobility and of the diffusion coefficient D, which can be obtained from the Einstein relation

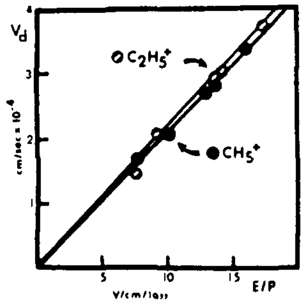

Figure 5. Variation of drift velocity of reactant ions in methane with E/P at 440 ± 5°K.

$$K/D = e/kT \qquad \text{(V)}$$

(provided that E/P is small) are shown in Table I. Experimental and theoretical diffusion coefficients, calculated from Langevin theory, are in substantial disagreement, confirming the inability to estimate residence times accurately from the simple equation (IV). Also shown in Table I are mean residence times and the number of collisions with neutral methane an ion undergoes during the period it remains in the ion source, on the assumption that the rate constant for the collision process is about 10^{-9} sec^{-1}. Rate constants for reactions of methanium and ethyl ion with additives of interest in chemical ionization studies should be substantially larger.

Under a particular set of experimental conditions discrimination toward the detection of different ionic species is governed entirely by the diffusion coefficient for each ionic species.[11,14] The identity of the observed diffusion coefficients for CH_5^+ and for $C_2H_5^+$ can there-

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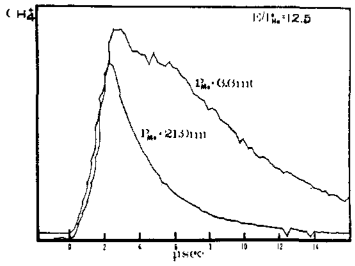

Figure 6. Arrival time distribution of methane ions in mixtures of 1.08 Torr helium and methane at 182°K.

fore not easily be ascribed to discrimination and could be the result of differences in the transport mechanism.[17-19]

B. Ion-Molecule Reaction Rate Constants from Drift Experiments. The ability to measure ion intensity directly as a function of reaction time (*i.e.*, ion residence time) provides a rapid, convenient, and accurate means of determining rate constants for ion-molecule reactions involving near-thermal ions. The only parameters which need to be known are pressure in the reaction region, temperature, and arrival time distributions with an accurate time scale. The approach can be used for chemical ionization systems but also generally for all types of ion-molecule reactions.

The reaction leading from reactant (primary) ion R^+ to product ions X_i^+ can generally be written as

$$R^+ + N \xrightarrow{k_1} \Sigma(X_i^+ + Y_i) \tag{1}$$

where N is the reactant neutral and Y_i the product neutrals. The total rate of reaction 1 is $-d[R^+]/dt = k_1[R^+][N]$, which yields on integration

$$\ln \frac{[R^+]}{[R_0^+]} = -kt([N_0] - [R_0^+]) + \ln\left(1 - \frac{[R_0^+] - [R^+]}{[N_0]}\right) \tag{VI}$$

Here $[R_0^+]$ is the initial concentration of reactant ions at zero time. Since the concentration of N is essentially invariant and much larger than $[R^+]$ the reaction is quasi first order and

$$\ln (R^+/R_0^+) = -k_1t[N] \tag{VII}$$

Since the decrease in reactant ion concentration is usually difficult to evaluate accurately, particularly when the pressure of reagent is changed, it has been customary to equate $R_0^+ = \Sigma X_i^+ + R^+$. t is obtained from eq IV, but the resultant rate constants are inconsistent between investigators[4,5] and vary with E/P.[5] This can probably be ascribed at least in part to the change in diffusion coefficient D with ion identity.

When arrival time distributions can be determined, however, R^+ is evaluated directly as a function of t. R_0^+ is still not readily accessible as a function of time, however, at two reactant concentrations N_1 and N_2

$$\ln (R_1^+/R_2^+) = \ln (R_{0,1}^+/R_{0,2}^+) - kt(N_1 - N_2) \tag{VIII}$$

As long as the initial ion arrival time distributions differ only in terms of intensity, the logarithmic term on the right hand side of eq VIII will be independent of t, and the logarithm of the ratio of reactant ion abundances at two pressures should be a linear function of t with slope $-k_1(N_1 - N_2)$. Knowledge of the ion transit time is not required since this quantity merely offsets the curve laterally. We believe that this method should be substantially free of the pitfalls of rate evaluations frequently encountered in such measurements.[20]

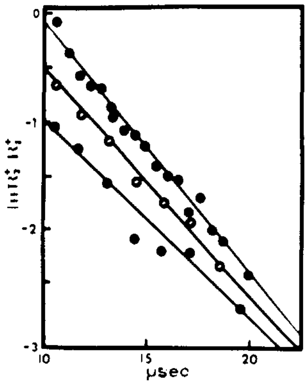

Figure 7. Evaluation of rate constant for reactions of CH_4^+ from eq VII at three values of E/P(He) (top to bottom): E/P(He) = 6.19, 5.12, and 1.25 V cm^{-1} Torr^{-1}; $\Delta P(CH_4)$ = 13.3, 16.6, and 15.1 mTorr.

The applicability of this approach was verified by examining the well-known reference reaction

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \tag{2}$$

Since this reaction is fast, small concentrations of reactant methane gas were introduced into the ion source already containing 1.08 Torr of helium as a drift or "bath" gas in the manner previously described by Vredenberg, *et al.*[5] Two representative methane ion arrival time distributions obtained at different methane pressures but under otherwise identical conditions are shown in Figure 6. The suppression of the high arrival time portion at the higher methane concentration is clearly evident. Three representative sets of data plotted according to eq VIII are shown in Figure 7. Rate constants derived from the least-squares fits of such graphs are shown in Table II. The variation of the rate constant with E/P reported elsewhere[5] is not observed, indicating that conditions in our experiment

Table II. Reaction Rate of CH_4^+ with CH_4 in Helium at 455 ± 3°K

E/P(He), V cm^{-1} Torr^{-1}	$P(CH_4)$, mTorr	$P'(CH_4)$, mTorr	ΔP, mTorr	$k \times 10^9$, cm^3 mol^{-1} sec^{-1}
1.25	9.3	24.4	15.1	1.05
2.00	7.4	24.0	16.7	1.00
3.69	10.3	21.9	16.6	1.03
5.12	6.3	22.9	16.6	0.89
6.19	8.3	21.6	13.3	0.99
9.08	10.6	21.6	10.8	0.98
12.5	6.6	21.9	15.3	1.04
				1.00 ± 0.04

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(19) S. L. Chong and J. L. Franklin, paper presented at the 19th Annual Meeting on Mass Spectrometry, Atlanta, Ga., May 1971; *J. Chem. Phys.*, **55**, 641 (1971).

(20) E. W. McDaniel, *ibid.*, **52**, 3931 (1970).

are well defined and that β is independent of ion energy as previously reported.[21] The only major sources of error are in the time interval measurement, which should be accurate to better than $\pm 5\%$, and in the determination of the concentration of reactant gas in the reaction region, which is probably accomplished within the same uncertainty. The absolute rate constant of $1.00 \pm 0.08 \times 10^{-9}$ cc sec^{-1} derived from these measurements is in good agreement with the value $1.09 \pm 0.09 \times 10^{-9}$ cc sec^{-1} reported by other investigators.[21]

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Rate Constants for Reaction of Hydrogen Atoms with Aromatic and Heterocyclic Compounds. The Electrophilic Nature of Hydrogen Atoms[1]

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Abstract: Rate constants for the reaction of H atoms with aromatic and nitrogen heterocyclic compounds in aqueous solutions have been measured by a steady-state *in situ* radiolysis–esr method. The rate constants for the aromatic compounds investigated vary between 2.4 and 26×10^8 M^{-1} sec^{-1} and those for the heterocyclic compounds between 0.6 and 3.3×10^8 M^{-1} sec^{-1}. Electron-donating substituents enhance the rate and electron-withdrawing groups retard the rate, qualitatively indicating an electrophilic character for the reaction. Correlation of the rate constants for a series of monosubstituted benzenes with Hammett's substituent constants shows a reasonably linear behavior ($\log k = 9.04 - 0.45\sigma$). Additivity of the σ constants was tested for the case of the acid form of the phenylenediamines and for the dicyanobenzenes. In the first instance the rate constants for all three isomers were found to be about one-half that for the anilinium ion, as expected from the Hammett plot. Additivity fails, however, in the case of the dicyanobenzenes where the rate constants for the three derivatives differ by a factor of two and those for the ortho and meta isomers are only slightly less than for cyanobenzene itself. In the case of pyridine the introduction of a nitrogen atom into the aromatic ring causes a considerable decrease in the rate constant. The effect of a second nitrogen atom is dependent on the position. The rate for pyrimidine is lower while the rates for pyridazine and pyrazine are higher than that for pyridine. These findings appear to reflect a reinforcement of the electron-withdrawing effect of the nitrogen atoms when they are in the 1 and 3 positions but a partial cancellation in the 1 and 2 or 1 and 4 positions.

It is known that, in general, aromatic compounds react with hydrogen atoms with rate constants of the order of 10^9 M^{-1} sec^{-1} and that the predominant pathway of this reaction is the addition to the aromatic ring.[2–8] Studies have been carried out by pulse radiolysis methods in which the formation of the cyclohexadienyl type radical was directly observed,[2–5] by competitive methods[6,7] and by a steady state esr method recently developed in these laboratories.[8,9] The former type of study specifically examines the addition reaction while the latter measures the total rate, but for most aromatic systems abstraction contributes little and the two types of measurements should give very similar rate constants. A previous intercomparison[6] of the relative rate constants for reaction of hydrogen atoms with the substituted aromatic compounds indicated that these rate constants could be correlated with the Hammett substituent constants and suggested an electrophilic behavior for the H atom in its attack on the aromatic ring. The rate constants measured were, in general, lower for compounds which had strong electron-withdrawing groups. These measurements were, however, made by a competitive method at pH 7 where the hydrogen atom yield is low and where precise measurements are difficult. The range of variation of rate constants was small and the deviations from a simple Hammett plot were relatively large. Recent pulse measurements, while generally giving rate constants which agreed with the competitive study, are not sufficiently extensive to corroborate the above suggestion. More detailed observations on the effect of substituents on the rate of reaction of hydrogen atom with aromatic systems are obviously in order. While either chemical competitive

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(1) Supported in part by the U. S. Atomic Energy Commission.

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