

Use of a phospholipid analogue of diphenyl-1,3,5-hexatriene to study vesicle fusion

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The synthesis of a phospholipid analogue of diphenyl-1,3,5-hexatriene (DPH) and its use to investigate melittin-induced phospholipid vesicle fusion are described.

The analogue has fluorescence properties that are appropriate to steady state and time-resolved studies of phospholipid aggregates and will not redistribute through the solution to bind to unlabelled material.

Phospholipid dispersions prepared in the presence of the analogue were examined as a function of temperature and the results were compared with those seen for DPH. In lipids below the characteristic phase transition temperature, the motion seen with both probes is similar, as judged by the depolarization of fluorescence. Above the transition temperature the analogue is more motionally restricted than DPH is.

The fluorescent phospholipid analogue should resolve some of the current uncertainties surrounding the parent chromophore. It is hoped that time-resolved measurements using synchrotron radiation will give information on the reported effects of malignancy and viral transformation on cell membranes.

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Time-resolved IR spectral photography

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The non-linear optics basis and experimental realization of time-resolved IR spectral photography (TRISP), a new technique of nanosecond time-resolved IR absorption spectroscopy, are described. TRISP has been applied to the study of transients. It was used to study the time evolution of the rotational temperature of HCl during CO₂-laser-induced explosions of HN₃-HCl mixtures. In a recent experiment *tert*-butyl radicals were formed by ruby laser photolysis of (CH₃)₃CNO. TRISP was used to obtain the gas phase IR spectrum of the

radicals in the $3\ \mu\text{m}$ region. By following the decay of this transient IR absorption, the rate coefficients for the combination and disproportionation reactions between *tert*-butyl radicals were deduced.

State-selective chemistry: the NCl radical

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The kinetics of the NCl radical were studied in a discharge flow system by molecular beam mass spectrometry. Ground $X\ ^3\Sigma^-$ state and metastable excited $a\ ^1\Delta$ and $b\ ^1\Sigma^+$ state NCl radicals were generated via the reaction of excess chlorine atoms with chlorine azide (N_3Cl): $\text{Cl} + \text{N}_3\text{Cl} \rightarrow \text{N}_3 + \text{Cl}_2$; $\text{Cl} + \text{N}_3 \rightarrow \text{NCl}^* + \text{N}_2$. The $a\ ^1\Delta$ and $b\ ^1\Sigma^+$ states of NCl were observed using the $a\ ^1\Delta-X\ ^3\Sigma^-$ ($1.07\ \mu\text{m}$) and $b\ ^1\Sigma^+-X\ ^3\Sigma^-$ (665 nm) transitions. On the addition of O_2 , the excited NCl^* radicals were quenched to the ground state. The formation of NCl_2 radicals was also observed in the $\text{Cl} + \text{N}_3\text{Cl}$ system. The addition of Cl_2 increased the NCl_2 concentration. However, the formation of NCl_2 could be completely suppressed by the addition of O_2 . It was deduced that the NCl_2 radicals were formed in the state-selective reaction of metastable excited state NCl^* radicals with Cl_2 : $\text{NCl}^* + \text{Cl}_2 \rightarrow \text{NCl}_2 + \text{Cl}$; $\text{NCl}(X\ ^3\Sigma^-) + \text{Cl}_2 \not\rightarrow \text{NCl}_2 + \text{Cl}$. Thus the kinetics of ground state NCl could be studied in the absence of excited NCl^* and NCl_2 by the addition of O_2 . Rate constants for the reactions $\text{NCl} + \text{NCl} \rightarrow \text{N}_2 + 2\text{Cl}$ and $\text{NCl} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{Cl}$ were determined, e.g. $k^{295}(\text{NCl} + \text{NO}) = (1.3 \pm 0.1) \times 10^{-11}\ \text{cm}^3\ \text{s}^{-1}$.

Direct determination of the rate constants of elementary reactions of atomic phosphorus using high sensitivity resonance fluorescence detection

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The reactions of ground state phosphorus atoms $\text{P}(3\ ^4\text{S}_{3/2})$ with the molecules O_2 , Cl_2 , NO , NO_2 and PCl_3 were studied by using the vacuum UV atomic resonance fluorescence technique in a flow system. $\text{P}(3\ ^4\text{S}_{3/2})$ was generated by microwave discharge of PCl_3 in the presence of excess helium carrier gas and the atomic resonance fluorescence was monitored using the 178.77, 178.29 and